# CARLSON ENVIRONMENTAL, INC.

June 7, 1999 PN 9566C

Mr. John O'Grady
Removal Project Manager
Office of Superfund (SR-6J0)
U.S. EPA Region 5
77 West Jackson Boulevard
Chicago, Illinois 60604

RE: QAPP Revisions
Fansteel, Inc.
Number One Tantalum Place
North Chicago, Illinois

Dear Mr. O'Grady:

Enclosed are the revisions to Great Lake Analytical's revisions to its Standard Operating Procedures (SOPs). These revisions are intended to address the comments and recommendations included in your letter to Mr. Clifton A. Lake dated May 6, 1999.

Carlson Environmental is simultaneously submitting revisions to its Quality Assurance Project Plan (QAPP), under separate cover.

Please feel free to contact me at (312) 704-8843 if you have any questions or comments as you review the enclosed materials.

Respectfully submitted,

CARLSON ENVIRONMENTAL, INC.

Margaret Karolyi

Margaret M. Karolyi, P.E.
Senior Project Manager

cc: Mr. Jonathan Jackson, Fansteel
Mr. Mark Steger, McBride, Baker & Coles

**ENCLOSURES**

Great Lakes Analytical Response Letter, May 28,1999

Standard Operating Procedure for Organochlorine Pesticides by Gas Chromatography: Capillary Column Method

Standard Operating Procedure for Synthetic Precipitation Leaching Procedure (SPLP)

Standard Operating Procedure for the Determination of pH

Standard Operating Procedure for the Determination of Total Solids, Total Dissolved Solids, Total Suspended Solids, Total Volatile Solids/Percent Ash, Fractional Organic Carbon, and ASTM Total Organic Carbon

Standard Operating Procedure for the Determination of Mercury in Liquids and Solids

Standard Operating Procedure for the Determination of Total Cyanide, Reactive Cyanide, and Cyanide Amenable to Chlorination in Liquids and Solids

Standard Operating Procedure for the Digestion of Liquids for the Analysis of Metals

Standard Operating Procedure (018) Method Clarification

Standard Operating Procedure for the Digestion of Solids for the Analysis of Metals

Standard Operating Procedure (018a) Method Clarification

Standard Operating Procedure for Analysis of Metals using GFAA

Standard Operating Procedure for Analysis of Metals using ICP

Metals Method Exception (37)

Standard Operating Procedure for Organic Extraction and Sample Preparation for Semivolatile Determinative Methods

Standard Operating Procedure for Polychlorinated Biphenyls by Gas Chromatography: Capillary Column Method

Standard Operating Procedure for the Determination of Volatile Organic Compounds by Purge-and-Trap and Gas Chromatography/Mass Spectrometry

Standard Operating Procedure for Polynuclear Aromatic Hydrocarbons by HPLC

GREAT LAKES ANALYTICAL

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May 28, 1999

Margaret Karolyi
Carlson Environmental, Inc.
65 East Wacker Place
Suite 1500
Chicago, Illinois 60601

Dear Ms. Karolyi,

Enclosed is the response to the EPA's comments on Great Lakes Analytical's standard operating procedures (SOPs) and performance data. The following outlines the actions taken to fulfill their requests:

**General Comments**

- SOPs are included for Pesticides, SPLP, pH, and TOC. Please note that SOP GLA 160.1/4 BG contains the procedure for TOC by ASTM Method D2974-87 and the procedure for determining percent dry weight.

**I. Control Limits**

A. The control limits for SPLP Pb are 78 – 114 % recovery for the LCS, and 77 – 113 % recovery for matrix spikes.

B. MDLs, PQLs, and RLs for VOCs, Pesticides, PNAs and PCBs are included in tables and are attached to the back of each SOP. Please note that the Action Level tables in the October 1998 SIWP do not reflect the correct reporting limits for some of the target analytes. Use the table submitted here as guidance for reporting limits.

**II. Mercury SOP GLA 245.1/5 BG**

A. MSA has been added to the SOP (Section 11.6.5).

B. The laboratory has always ended each analytical run with a calibration blank and check standard. The SOP has been revised to include this step in the procedure (Section 11.6.3).

C. The equations for %Rec and RPD calculations have been added (Sections 11.7.3 and 11.7.4).

**III. Total Cyanide SOP GLA335.4 BG**

A. MSA has been added to the SOP (Section 6.7).

B. The laboratory has always ended each analytical run with a calibration blank and check standard. The SOP has been revised to include this step in the procedure (Section 11.7.5).

C. The equations for %Rec and RPD calculations have been added (Sections 11.8.4 and 11.8.5).

**IV. Digestion of Liquids SOP GLA 3050 BG**

A. Tantalum (Ta) is going to be analyzed by one of our network laboratories, Sequoia Analytical in Walnut Creek, California. A copy of their SOP for liquid digestions is included (SOP 018).

B. A table has been added to the SOP (Appendix B) that specifies the components of each standard solution.

**V. Digestion of Solids SOP GLA 3050 BG**

A. Tantalum (Ta) is going to be analyzed by one of our network laboratories, Sequoia Analytical in Walnut Creek, California. A copy of their SOP for solids digestions is included (SOP 018a).

B. Discussion of the preparation of the LCS and a reference to the % dry weight determination has be included (Section 11.3).

C. Silver (Ag) has been added to Section 11.4.

D. A table has been added to the SOP (Appendix B) that specifies the components of each standard solution.

**VI. Metals by Graphite Furnace SOP GLA 7000 BG**

A. The concentrations of the calibration standards has been added (Section 11.2.1)

B. The recommended instrument parameters have been added (Section 11.1).

C. MSA has been added to the SOP (Section 11.3.5).

D. The equations for %Rec and RPD calculations have been added (Sections 11.4.3 and 11.4.4).

**VII. Metals by ICP SOP GLA 6010 BG**

A. MSA has been added to the SOP (Section 11.4.8).

B. The laboratory has always ended each analytical run with a calibration blank and check standard. The SOP has been revised to include this step in the procedure (Section 11.4.7).

C. The equations for %Rec and RPD calculations have been added (Sections 11.5.3 and 11.5.4).

**Note:** A copy of Sequoia Analytical's ICP SOP has been included for the analysis of Ta.

**VIII. Organic Extractions SOP GLA 3500 BG**

A. The determination of % dry weight has been referenced in the SOP (Section 13.3.12).

B. The laboratory does obtain adequate performance using methylene chloride as the extraction solvent for solids. However, a mixture of acetone/methylene chloride is used when extracting solid sample for pesticides and PCBs.

C. The laboratory does obtain adequate performance with a final extract volume of 10 ml for Method 8310 (refer to the MDL table at the back of SOP GLA 8310BG).

**IX. PCBs by GC SOP GLA 8082 BG**

A. Each analytical run ends with a check standard. This has been added to the SOP (Section 6.3).

B. Surrogate standards are now prepared in acetone. This has been changed in the SOP (Section 10.1.1).

C. The concentrations of the calibration standards has been added (Section 8.1).

D. The confirmation analysis of PCBs follows the same stringent calibration and QC requirements as the primary analysis (See Section 6.6).

E. The equations for %Rec and RPD calculations have been added (Sections 11.5.5 and 11.5.6).

F. The % dry weight has been added to the equation for calculating final results of solids (Section 11.5.3).

G. The typo was fixed. Moreover, Section 11.5.4 has been added to discuss the reporting of detections above the MDL but below the RL.

**X. Analysis of Volatiles SOP GLA 8260 BG**

A. As mentioned above, a table including the MDLs, PQLs, and RLs has been added to the back of the SOP. This table also includes retention times.

B. A description of the mass spectrometer parameters has been added (Section 9.3). The laboratory does not currently perform SIM analyses.

C. The concentration of the calibration standards has been included (Section 8.1.1).

D. Refer to the MDL table mentioned above.

E. Detects above the MDL but below the RL can be reported upon client request.

F. Methyl iodide has been included in the primary characteristic ion table.

**XI. PNAs by HPLC SOP GLA 8310 BG**

A. As mentioned above, a table including the MDLs, PQLs, and RLs has been added to the back of the SOP. Appendix A includes retention times.

B. Fluorene has been added to the requested table.

C. The concentration of the calibration standards has been added (Section 10.1.2).

D. More discussion on the calibration procedures has been included (Sections 8.1 and 10.1.2).

E. A description of the gradient program is included (Section 11.1).

F. The equations for %Rec and RPD calculations have been added (Sections 11.5.1 and 11.5.2).

Please let me know if you have any questions or concerns. Have a great day!

Sincerely,

James Knapp
*Quality Assurance Manager*
Email : jknapp@glalabs.com

Enclosures

Copy #: 8081-____

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY:

## CAPILLARY COLUMN METHOD

## GLA 8081 BG

Revision 1.1

Approved By:

Department Manager: _____ Date: 5-28-99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Manager: _____ Date: 5/28/99

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of organochlorine pesticides and related compounds by capillary gas chromatography (GC). This SOP is an interpretation of EPA method 8081A. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

## 1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples. (Note: use method 8082 for samples for PCB - polychlorinated biphenyl - analysis.) Chlordane and toxaphene are listed as multi-component target analytes. If the matrix of these samples were environmentally degraded (*i.e.* "weathered"), pattern recognition of these analytes may require more detailed study.

## 1.2 REGULATORY APPLICABILITY

40 CFR 121

# 2.0 SUMMARY

Samples for pesticide analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, GLA SOP 3500 BG, sections 11.1 and 11.3). If necessary, solvent exchange to hexane or isooctane must be performed. Extracts are stored under refrigeration and must be analyzed within 40 days of extraction.

Extracts are analyzed by capillary gas chromatography with electron capture detection (ECD). Electrolytic conductivity detection (ELCD) may also be used. The GC is standardized to determine the recovery and limits of detection for the analytes of interest. Sample concentrations are determined by comparison to standard responses. Quantitative analysis is achieved through measurements of peak heights or integrations of peak areas.

Organochlorine pesticides that can be detected by this method include: aldrin, α-BHC, β-BHC, γ-BHC (lindane), δ-BHC, technical chlordane (including α-chlordane and γ-chlordane), 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, diallate, dieldrin, endosulfans I and II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, isodrin, kepone, methoxychlor, and toxaphene. Other compounds that may be detected include: alachlor, captafol, chloroneb, DCPA, dichlone, dicofol, halowax materials, nitrofen, PCNB, perthane, strobane, permethrin, and trifluralin.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents.

### 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

### 3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

### 3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants at high levels. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

## 4.0 INTERFERENCES

### 4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

### 4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

### 4.3 COEXTRACTED INTERFERENCES

Materials causing interferences may be coextracted from a sample. The extent of matrix interferences varies from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

### 4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe or purging device should be rinsed out between samples with water or solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or water to check for cross contamination.

### 4.5 CHROMATOGRAPHY

Coelution among the target analytes may cause interference. For example, DDD and endosulfate II coelute on a DB 608 column, methoxychlor and endosulfan sulfate coelute on a DB1701 column. If this is suspected, standards of the individual analytes may be analyzed and retention times compared.

Carbophenothion, dichlone, dichloran, nitrofen, and kepone may exhibit extensive peak tailing. Atrazine and simazine may give poor responses on the ECD detector. Triazine compounds should be analyzed using Method 8141 (with NPD option).

### 4.5 SULFUR

The presence of sulfur produces a large broad peak that interferes with the detection of early to middle eluting analytes. Sulfur contamination should be expected with sediment samples. Since the recovery of sulfur-containing pesticides (*e.g.* endosulfan, endrin aldehyde) is reduced during sulfur cleanup, these compounds are determined prior to cleanup.

### 4.6 INDUSTRIAL CHEMICALS

Other pesticides and industrial chemicals (*e.g.* PCBs) may cause interferences. Some coeluting organophosphorous pesticides can be removed using gel permeation chromatography (GPC) cleanup. Chlorophenols may be removed using florisil cleanup.

## 5.0 RECORD KEEPING

### 5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.

### 5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each method. It has the method identification number on the outside cover. The contents of each book include:

- Copy of the GLA Quality Assurance Program manual.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and the internal standard control limits and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.

## 5.3 RUN LOG

The front cover of the Run Log notebook displays:
- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:
- Calculations represented with a generic calculation.
- The names and concentrations of the internal standard and surrogate standard(s).

The following column headings are written at the top of each page:
- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used.
- Matrix type.
- Surrogate standard percent recoveries.
- Results complete with units.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:
- Quality control function (check standard, blank, matrix spike, etc.)
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed. Laboratory notebooks must be neat and legible. Mistakes and crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out.

## 5.4 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all standards prepared for the method. Document in the book:
- Analyte, purpose (method, calibration, internal, etc.).
- Supplier.
- Lot number.
- Initial concentration of the stock solution.
- Expiration date of stock standard - 3 months after the standard has been opened, or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards:
- Volume diluted.
- Volume prepared.
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code for the final solution. The GLA code is a number letter sequence used to track standard preparations within the lab. It consists of the month number and successive letter of the alphabet, starting with "A" at the beginning of each month.

# 6.0 QUALITY CONTROL

## 6.1 METHOD BLANKS

Method Blanks are prepared and analyzed to check for any laboratory contamination. For each matrix-specific extraction batch, a method blank is prepared. The method blank is taken through the identical extraction steps as the samples. Deionized water and clean sand are used as the blank matrix for water and soil, respectively. No target analytes should be detected above the requested reporting limit. If target analytes are detected in the method blank, and the same target analytes are not found in the samples, no corrective action is taken. If target analytes are detected in the method blank, and the same target analytes are found in the samples, all associated samples and QC are either reextracted, or the results are qualified.

## 6.2 CHECK STANDARD

Check standards validate the initial calibration curve and is used to gauge the daily operating condition of the instrument. It must be from a different supplier than the calibration standard. The check standards contain the analytes at concentrations of 1 to 100 µg/L. The compounds are quantitated using the average RF for each compound calculated in the calibration study.

The recovery of each analyte in the check standard must be between 85 and 115%.

$$Recovery\ (\%) = \frac{calculated\ concentration}{concentration\ analyzed} \times 100$$

A check standard is analyzed once every 20 samples, or 12 hours, whichever occurs first. The check standard is used to check chromatography for peak shape or co-elution problems. The check standard must be quantitated before the samples in the sequence to verify that the samples are being quantitated against a valid calibration. Recoveries of all check standard analytes are documented in tables for tabulation of yearly statistical recovery limits. Samples must be bracketed by a valid check standard.

## 6.3 CHECK BLANK

The check blank verifies that the analytical system is free from contamination. No contamination should be present in the blank above the reporting limit. A check blank sample is analyzed once every 20 reportable samples. The check blank must be quantitated before samples to verify that the system is "clean". If contamination is found, samples run in that analysis sequence that contain the same contaminant are reanalyzed with a clean blank to confirm results.

## 6.4 SURROGATE STANDARD

Surrogate standards are used to monitor the efficiency of the procedure. The surrogate standard for this method is decachlorobiphenyl (TMX = 0.4 µg/mL DCB = 0.3 µg/mL in check standard and 0.5 µg/mL in samples for both). The surrogate standard recoveries are tracked from all standards and samples over a year to determine control limits. These limits are defined as the average recovery plus/minus 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

## 6.5 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are extracted and analyzed regularly to check the effect of the sample matrix on the performance of the method. The MS/MSD is a measure of the accuracy and precision of the method. Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates.

6.5.1 An MS/MSD is extracted and analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes samples are spiked with all target compounds (except toxaphene and methoxychlor) at a final concentration of 3.3 µg/Kg and 0.1 µg/L, respectively.

6.5.2 Spike recoveries and percent differences of the duplicates for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries and percent differences must fall within the average spike recovery and percent difference over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 10 sets of MS/MSDs. These limits should be posted by the analyst for reference.

## 6.6 LABORATORY CONTROL SPIKES

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

6.6.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) are spiked with all target compounds (except toxaphene and methoxychlor) at a final concentration of 3.3 µg/Kg and 0.1 µg/L, respectively.

6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 LCSs. These limits should be posted by the analyst for reference.

For those extraction batches that do not have sufficient sample volume to extract the matrix spike in duplicate, the LCS is extracted in duplicate.

## 6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- Recovery for check standard fails for a particular compound that was present in the sample.
- Decomposition of endrin or DDT exceeds 15%.
- Contamination was present in the blank and in the sample.
- Recovery for QC samples outside of limits.

## 6.8 CONFIRMATION

All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (*i.e.* dissimilar stationary phase to primary column) to verify the presence of the analyte(s). All QC requirements, including calibrations and retention times for the confirmation analyses must be fulfilled. If sensitivity permits, GC/MS method 8270 may be used for confirmation.

## 6.9 DATA REVIEW

Data obtained by this method are reviewed by another analyst or a supervisor to ensure accuracy of results. (See Data Review Checklist attached to this SOP.)

# 7.0 SAMPLE MANAGEMENT

**7.1** The procedure for sample management are detailed in the Great Lakes Analytical SOP for *sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions* and preparations for analytical batches.

**7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8081 are queued under "EXTR" and "PEST". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

# 8.0 METHOD VALIDATION

## 8.1 CALIBRATION STUDY

A calibration study determines the response factors (RFs) for analytes that are used for the determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram. The calibration standard concentrations are 0.05, 0.1, 0.2, 0.5, 0.75, and 1.0 µg/ml. Single point calibrations are performed for multi-component compounds such as toxaphene and technical chlordane.

A response factors (RF) is calculated by tabulating responses of each analyte against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than 20%, linear regression is used to establish the equation of the calibration curve for that particular compound: *peak area = slope × concentration + constant.* Linear regression is valid only if the correlation coefficient ($r^2$) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. Add 0.5 µg/mL of surrogate standard to each level.
- For each compound, calculate:
  - $RF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$
  - *Average and standard deviation for RFs*
  - $\%RSD = \frac{\text{standard deviation of RFs}}{\text{average RF}} \times 100$
- If the %RSD is less than 20%, the average RF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater.
- Check standards are analyzed following a calibration study.
- Recovery for the check standards must be between 80 and 120%.

### 8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the recoveries of 7 aliquots times the t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 aliquots is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if you inject 1µg/L of standard, the calculated MDL must be between 0.1 and 1 µg/L. A MDL study is done annually.

Procedure summary:

- Analyze 7 replicates of low level standard (at or below lowest calibration level standard).
- Calculate standard deviation for the 7 replicates.
- MDL = standard deviation × 3.143.
- The calculated MDL must be less than the reporting limit.

**Note:** MDL studies for multi-component compounds (technical chlordane, toxaphene) are defined as the lowest concentration for which pattern recognition is possible.

### 8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed annually, or when a new column is installed.

Procedure summary:

- Analyze the check standard three times over a 3 day period.
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time ± 3 × standard deviation. (A standard deviation of 0.01 may be used if the calculated standard deviation is less than 0.01 minutes.)
- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

### 8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy (demonstration of proficiency).

Procedure summary:

- Analyze 4 replicate standards or spiked extracts.
- Recoveries of each compound must be between 80 and 120%
- The %RSD must be less than 20%.

## 9.0 EQUIPMENT

9.1 Gas chromatograph, consisting of:

- Column oven, electron capture detector (ECD) - Hewlett Packard 5890 or equivalent.
- Sample injector/controller - Hewlett Packard 7672 or equivalent.
- Analytical column - 30 m × 0.53 mm, DB-608 (J&W Scientific, no. 125-6837, or equivalent); for confirmation - 30 m × 0.25 mm, DB-XLB (J&W Scientific no. 122-1232, or 30 m × 0.53 mm 0.5 µm XTI-5, or equivalent).
- Data collection and analysis system.

9.2 Glass syringes, various sizes.
9.3 Volumetric flasks, various sizes.

## 10.0 STANDARDS AND REAGENTS

### 10.1 STANDARD SOURCES

Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Examples include:

10.1.1 Surrogate standard for samples - Restek Pesticide Surrogate Mix (no. 32000): decachlorobiphenyl (200 µg/mL); dilute 250 µL to 100 mL with hexane; for waste dilution samples, dilute 750 µL to 25 mL.

10.1.2 Spike standards - Restek 608 Pesticide Calibration Mix (no. 32022): xxx; dilute 50 µL to 100 mL with hexane.

10.1.3 Analytical method standards -

A. Restek Pesticide Standard Mix A (no. 32003): α-BHC, γ-BHC, endosulfan I, heptachlor, 2,4,5,6-tetrachloro-m-xylene (each 8 µg/mL), DDD, DDT, decachlorobiphenyl, dieldrin, endrin (each 16 µg/mL), methoxychlor (80 µg/mL); dilute for a final concentration of 0.1 µg/mL (of each component).

B. Restek Pesticide Standard Mix B (no. 32004): aldrin, β-BHC, δ-BHC, α-chlordane, γ-chlordane, heptachlor epoxide, 2,4,5,6-tetrachloro-m-xylene (each 8 µg/mL), DDE, decachlorobiphenyl, endosulfan II, endosulfan sulfate, endrin aldehyde, endrin ketone (each 16 µg/mL); dilute for a final concentration of 0.1 or 0.2 µg/mL (for the corresponding 8 and 16 µg/mL components).

C. Restek Pesticide Evaluation Mix (no. 32032): aldrin, dibutyl chlorendate, DDT, endrin (each 100 µg/mL); dilute for a final concentration of 1.0 µg/mL (of each component).

10.1.4 Final pesticide spike -
Supelco TCL Pesticides Mix (no. 4-8913): aldrin, α-BHC, β-BHC, γ-BHC, δ-BHC, DDD, DDE, DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, endrin ketone, heptachlor, heptachlor epoxide, methoxychlor (each 2000 µg/mL); dilute for a final concentration of 0.1 µ.g/mL (of each component).

**Note:** Standard solutions should be stored protected from light exposure at approximately 4°C in Teflon-sealed containers.

**Note:** β-BHC, dieldrin, and some other standards may not be adequately soluble in hexane. A small amount of acetone or toluene may be used to dissolve these compounds during preparation of the standard solutions.

**Note:** Although all single component analytes can be resolved on a new column, two calibration mixtures can be prepared to minimize potential resolution and quantitation problems on older columns and during confirmation analyses. Separate calibration standards are required for each multi-component target analyte (*e.g.* toxaphene and methoxychlor).

**Note:** Compounds are also individually available.

### 10.2 STANDARD DILUTIONS

Stock and working standards should be kept in a refrigerator between 0 and 10°C when not in use to preserve their integrity. **Do not freeze!**

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

$C_1$ = concentration of the stock standard.
$C_2$ = desired or calculated concentration of the working standard.
$V_1$ = volume of the stock standard diluted.
$V_2$ = volume of working standard prepared.

## 10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description.
- Manufacturer.
- Lot number.
- Concentration.
- Date opened.
- Expiration date.

Place vial in refrigerator. The stock standard expires 6 months after opening, or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Standard Log.

## 10.4 WORKING STANDARD

Standards are prepared in hexane.

- Determine volumes of stock and working standard required.
- Fill volumetric flask about ¾ full with hexane.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to vial with "mini-nert" cap.
- Label vial with:
  - Analyte description.
  - Concentration of standard.
  - Date prepared.
  - Purpose (method).
  - Initials.
  - Expiration date.
  - GLA code.

The working standard expires 6 months after opening, or when the standard fails QC criteria, whichever is first. Preparation is documented in the Standard Log.

NOTE: A 5µL aliquot of a 10 ng/µL working standard is equivalent to 50 ng:
*10 ng/µL x 5 µL = 50 ng*

## 10.5 REAGENTS

10.5.1 Hexane - pesticide grade or equivalent.
10.5.2 Helium - ultra-high purity grade.
10.5.3 Nitrogen - ultra-high purity grade.

## 11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions.

### 11.1 ANALYTICAL SEQUENCE

Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. Calibration of all target analytes must be verified at a minimum of every 12 hours. The calibration factor for each analyte must not exceed a 15% difference when compared to the initial calibration curve.

Example Analytical Sequence:

- Check blank
- Check standard
- No more than 10 samples
- Method spike
- No more than 10 samples
- Method spike duplicate

### 11.2 RETENTION TIME WINDOWS

11.2.1 Retention time windows are established daily for each analyte. Use the retention times for each analyte in the check standards as the midpoints of the windows. The daily retention time windows are the midpoints plus/minus 3 times the standard deviation (determined in section 8.3). See Appendix A for an example chromatogram.

11.2.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (dissimilar stationary phase) to verify the presence of the analyte(s). Another technique, such as GC/MS, may be used (see section 11.7).

### 11.3 GAS CHROMATOGRAPHIC ANALYSIS

11.3.1 GC Operating conditions:

Temperature parameters

Injector: 250°C
Detector: 320°C
Oven program: 50°C for 1 min
50 to 100°C at 25°C/min (2 min)
100 to 320°C at 10°C/min (22 min)
320°C for 1 min
Alternate program for confirmation column:
140°C for 2 min
140 to 240°C at 10°C/min (10 min)
240°C for 8 min
240 to 260°C at 2.5°C/min (8 min)
260°C for 1 min
260 to 280°C at 15°C/min (1.3 min)
280°C for 10 min

Gas flow

| | |
|---|---|
| Column | ~5 mL/min |
| Make-up | ~50 mL/min |

Injection

| | |
|---|---|
| Volume | 2 µL, splitless |

The GC column should be conditioned before every pesticide run by injecting a pesticide standard at a concentration of approximately 20 times the daily calibration check. Several analytes, including Aldrin, may be observed in the injection just following this system priming - run an acceptable blank prior to running any standards or samples.

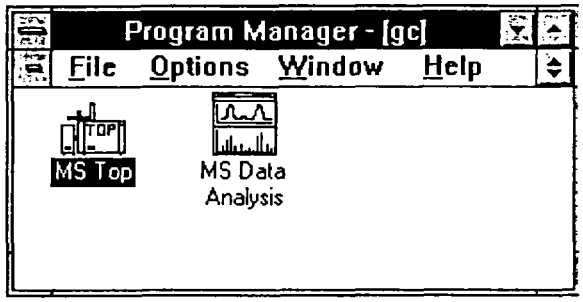
The amount of chemical decomposition of endrin and DDT that occurs within the GC system must be monitored. A standard containing endrin and DDT at concentrations within the calibration range is analyzed. If the amount of decomposition exceeds 15%, take corrective action - usually injection port maintenance.

An initial oven temperature of 140-150°C is required for resolution of the 4 BHC isomers. A final temperature of 240-270°C is required for elution of decachlorobiphenyl.

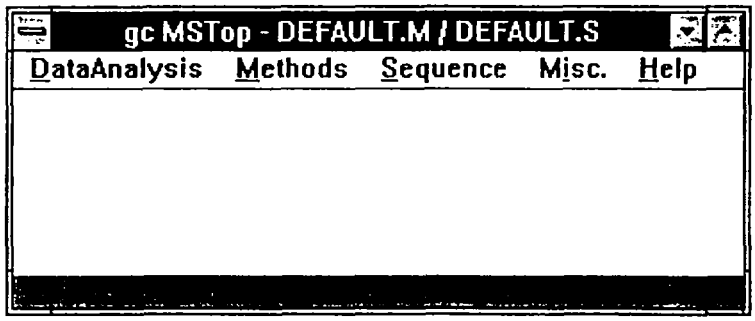
Because of the sensitivity of the ECD detector, the injection port and column should be cleaned prior to calibration.

## 11.4 SETTING UP A SEQUENCE IN ENVIROQUANT

In Program Manager there is a group called GC-Enviroquant or GC/MS-#. Using the mouse, double click to open it and there will be an icon that looks like a GC.




Double click on the GC icon to open it.

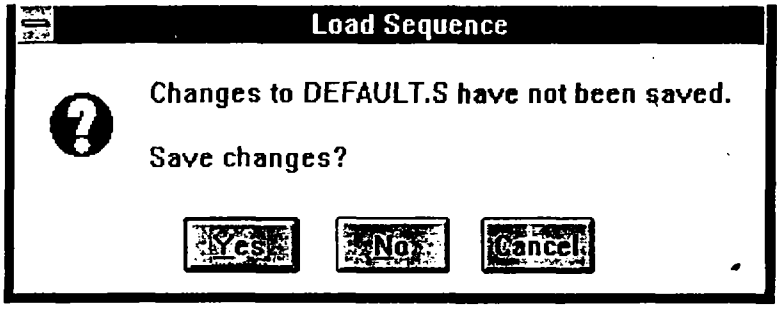



Click on the "Sequence" menu item and drag pointer to "Edit Sample Log Table".

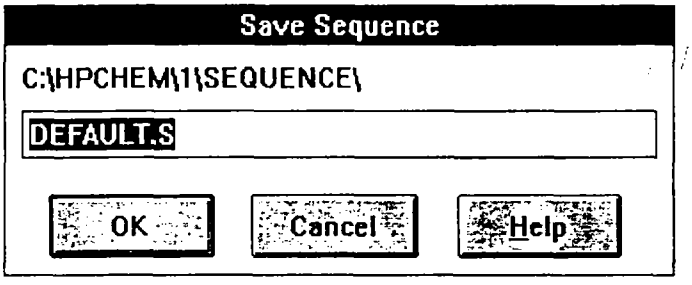
Enter the sample information for each sample including Data File name, Method, and Sample Name.
The sample name is the LIMS information, which will look like:

GLA sample number|PEST|8081|OK

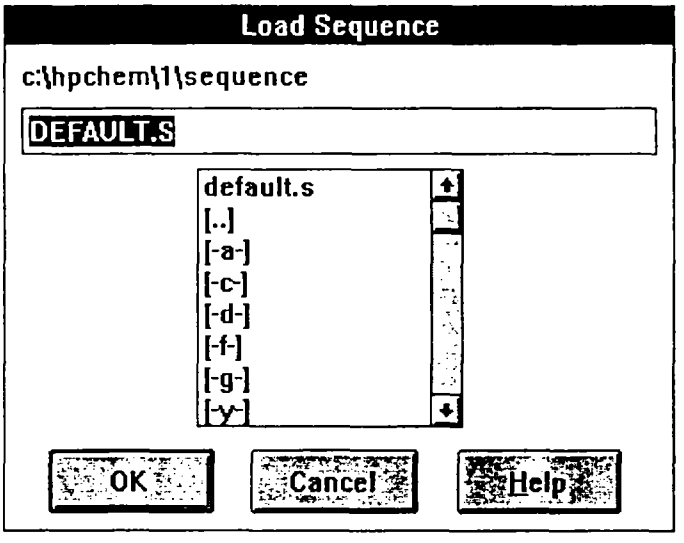
Leave the miscellaneous field empty.
When this is done click on OK.
Go back to the "Sequence" menu and drag to "Load and Run Sequence".



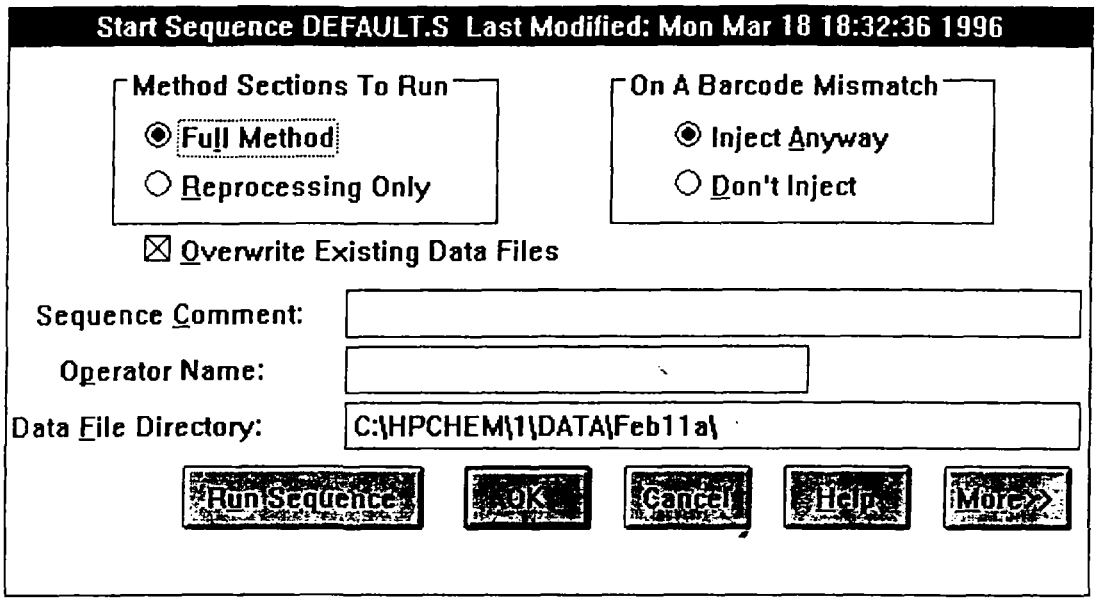

Click on "Yes".




Click on "OK".




Click on "OK".




In the "Method Sections To Run" box, the circle next to "Full Method" should be filled in.
In the "On A Barcode Mismatch" box, the circle next to "Inject Anyway" should be filled in.
The box next to "Overwrite Existing Data Files" should be checked.
In the "Operator Name" box, the analyst's initials that are used in LIMS are added.
In the "Data File Directory" field, after \DATA\, enter today's date or if the sequence was interrupted enter today's date with a letter appendage.
Click on Run Sequence.

## 11.5 QUANTITATION

11.5.1 If the responses exceed the linear range of the system, dilute the extract and reanalyze. If peak detection is prevented by the presence of interferences, further cleanup is required.

11.5.2 The concentration of each analyte in the sample is determined by calculating the amount of standard injected, from the peak response, using the response factor (RF) or linear regression calibration curve (section 8.1). These calculations may be done directly by the data collection and analysis software.

For aqueous samples:

*Concentrations determined manually -*

$$\text{Concentration } (\mu g/L) = \frac{A_x \times V_t \times D \times 1000}{CF \times V_s} \quad \text{or} \quad \frac{(A_x - C) \times V_t \times D \times 1000}{S \times V_s}$$

Where:

$A_x$ = peak area response for the analyte in the sample.
CF = average calibration factor.
$V_t$ = volume of total extract (1 mL).
$V_s$ = volume of sample extracted (1000 mL).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting liters to milliliters.
C = linear regression constant.
S = linear regression slope.

*Concentrations determined by software -*

$$\text{Concentration } (\mu g/L) = \frac{R_x \times V_t \times D \times 1000}{V_s}$$

Where:

$R_x$ = average concentration reported for sample, in µg (divide result by 1000 if concentration reported as mg).
$V_t$ = volume of total extract (1 mL).
$V_s$ = volume of sample extracted (1000 mL).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting liters to milliliters.

For soil/solid samples:

*Concentrations determined manually -*

$$\text{Concentration } (\mu g/kg) = \frac{A_x \times V_t \times D \times X \times 1000}{CF \times W} \quad \text{or} \quad \frac{(A_x - C) \times V_t \times D \times X \times 1000}{S \times V_s}$$

Where:

$A_x$ = peak area response for the analyte in the sample.
CF = average calibration factor.
$V_t$ = volume of total extract (1 mL).
W = weight of sample extracted (30 g).
D = dilution factor (if no dilution was made, D = 1).
X= Percent solids (in decimal form; ex., 90%=0.90)
1000 = factor converting kilograms to grams.
C = linear regression constant.
S = linear regression slope.

*Concentrations determined by software -*

$$\text{Concentration } (\mu g/kg) = \frac{R_x \times V_t \times D \times 1000}{W}$$

Where:

$R_x$ = average concentration reported for sample, in µg (divide result by 1000 if concentration reported as mg).
$V_t$ = volume of total extract (1 mL).
W = weight of sample extracted (30 g).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting kilograms to grams.

11.5.4 If an analyte is not present or present below the reporting limit (RL), report the result as N.D. or "non-detected". However, upon request, analytes detected above the method detection limit (MDL) but below the RL are reported as estimated.

11.5.5 Percent Recovery Calculation for spiked samples and LCS:

$$\%\text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.5.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of 1}^{st}\text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of 1}^{st}\text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

## 11.6 MULTI-COMPONENT ANALYTES

Multi-component analytes present problems in measurement. See Appendix B for suggestions for handing toxaphene, strobane, chordane, BHC, and DDT.

## 11.7 GC/MS CONFIRMATION

11.7.1 GC/MS confirmation may be used in conjunction with either single-column or dual-column analysis if the concentration is sufficient for detection. Full-scan GC/MS will normally require a concentration of approximately 10 ng/µL in the final extract for each single-component compound. Ion trap or selected ion monitoring will normally require a concentration of approximately 1 ng/µL. GC/MS confirmation may not be used for concentrations less than 1 ng/µL. A QC reference sample containing the compounds of interest must be analyzed by GC/MS. The concentration of the QC sample must demonstrate that those pesticides identified by GC/ECD can be confirmed.

11.7.2 GC/MS confirmation should be accomplished by analysis of the same extract that was used for GC/ECD and the associated method blank extract on a calibrated GC/MS instrument. The base/neutral/acid extract and associated blank may be used if the surrogates and internal standards do not interfere and it is demonstrated that the analyte is stable during acid/base partitioning. If the compounds are not detected in the base/neutral/acid extract, the GC/MS analysis of the pesticide extract should be performed.

## 11.8 REPORTING OF RESULTS

11.8.1 For compound hits that have been confirmed (and are above detection limits):

For aqueous samples:

$$\text{Concentration } (\mu g/L) = \frac{\text{amount } (\mu g)}{\text{sample}} \times \frac{\text{1 sample}}{\text{1000 mL}} \times \frac{\text{1000 mL}}{\text{L}}$$

For soil/solid samples:

$$\text{Concentration } (\mu g/kg) = \frac{\text{amount } (\mu g)}{\text{sample}} \times \frac{\text{1 sample}}{\text{30 g}} \times \frac{\text{1000 g}}{\text{g}}$$

11.8.2 If an analyte is not present or present below the reporting limit, report the result as N.D. or "non-detected".

11.8.3 Sequences are moved to the reviewed directory on the computer hard drive. The data is reprocessed for the creation of a ".csv" file and this is parsed to the LIMS:

- Go to "tools".
- Go to "do list".
- Quant to forms without cal.
- (OK) -> choose
- Highlight desired files using mouse, and then choose "cancel". Then the next "OK" and files will be created.

# 12.0 MAINTENANCE AND TROUBLESHOOTING

## 12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

## 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

## 12.4 COLUMN INSTALLATION

Column re-installation is necessary whenever maintenance is performed to the injection or detection ports. A new column is required when the baseline is elevated or the chromatography is poor.

For column installation, first slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to ensure that there are no jagged edges. The proper lengths of the column (to the base of the ferrule nuts) to be inserted into the injection and detection ports are 27 mm and 72 mm, respectively. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. Tighten the nuts - do not overtighten - make sure the graphite ferrule is seated and not "smashed".

New columns must be conditioned before method validation: Leave the column disconnected from the detection port. Ramp the oven temperature up to just below its maximum, at 1°C/min, and hold for 4 hours.

# 13.0 REFERENCES

13.1 EPA Method 8000B: Gas Chromatography.
13.2 EPA Method 8081A: Organochlorine Pesticides by Capillary Column Gas Chromatography.
13.3 Great Lakes Analytical Quality Assurance Program manual.
13.4 Great Lakes Analytical Chemical Hygiene Plan.
13.5 Great Lakes Analytical SOP for Login Department.
13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

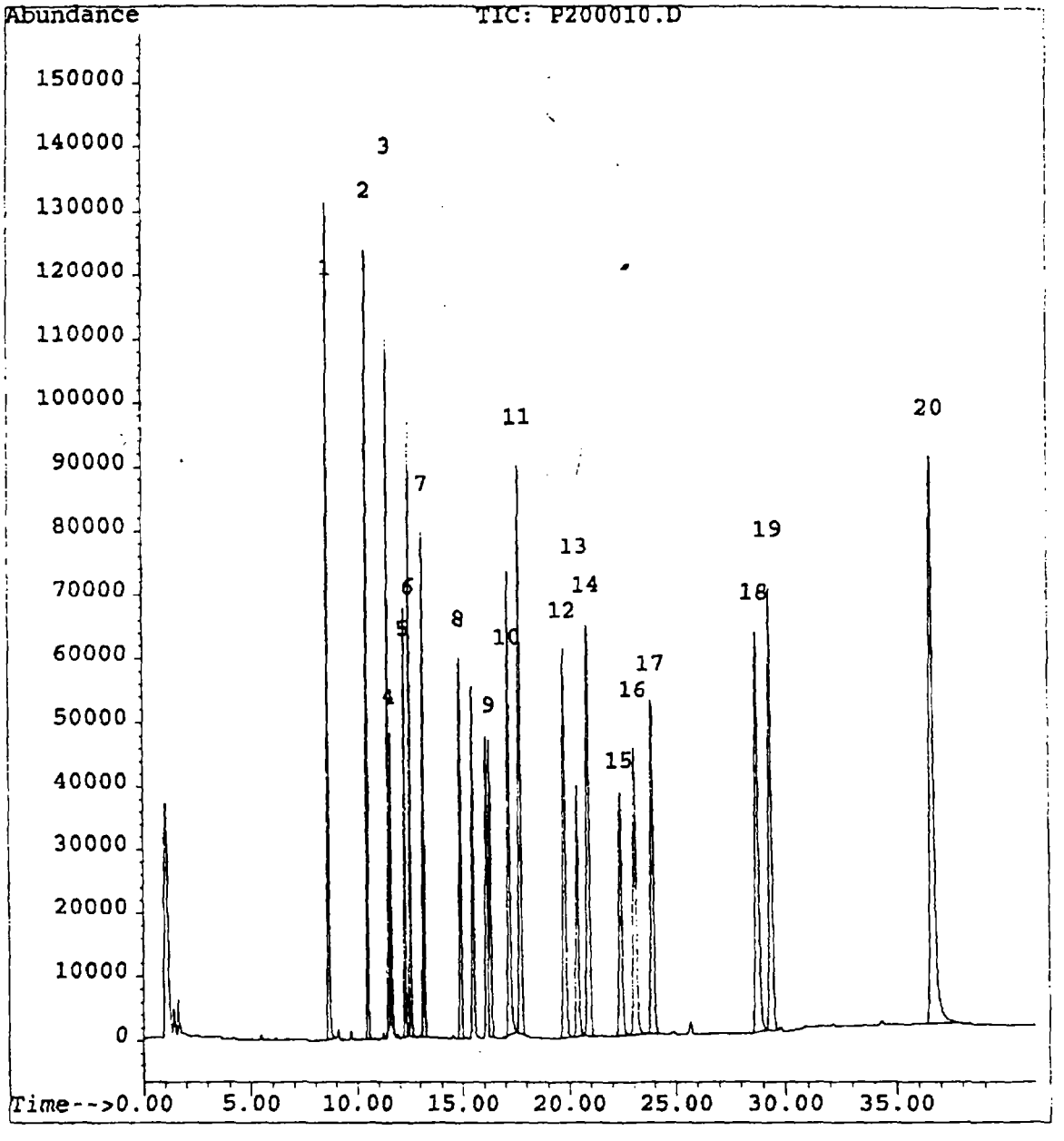
# 14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual.

# APPENDIX A.

## EXAMPLE CHROMATOGRAM.

| Peak No. | Compound | Approximate R.T. (min) | Response (area counts × $10^6$) |
|---|---|---|---|
| 1 | Tetrachloro-m-xylene | 8.6 | 5.7 |
| 2 | α-BHC | 10.5 | 4.6 |
| 3 | γ-BHC (lindane) | 11.5 | 3.8 |
| 4 | β-BHC | 11.6 | 1.6 |
| 5 | Heptachlor | 12.3 | 2.7 |
| 6 | δ-BHC | 12.5 | 3.6 |
| 7 | Aldrin | 13.2 | 3.6 |
| 8 | Heptachlor epoxide | 14.9 | 3.2 |
| 9 | Endosulfan I | 16.3 | 2.8 |
| 10 | 4,4'-DDE | 17.2 | 5.2 |
| 11 | Dieldrin | 17.7 | 6.3 |
| 12 | Endrin | 19.8 | 5.1 |
| 13 | 4-4'-DDD | 20.4 | 3.3 |
| 14 | Endosulfan II | 20.9 | 5.6 |
| 15 | 4-4'-DDT | 22.4 | 3.3 |
| 16 | Endrin aldehyde | 23.1 | 4.3 |
| 17 | Endosulfan sulfate | 23.9 | 4.8 |
| 18 | Methoxychlor | 28.8 | 6.3 |
| 19 | Endrin ketone | 29.4 | 6.2 |
| 20 | Decachlorobiphenyl | 36.6 | 11.1 |


Abundance
TIC: P200010.D
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
Time-->0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00

# APPENDIX B.

## ANALYSIS OF MULTI-COMPONENT ANALYTES.

A.1 **Toxaphene** - Toxaphene is manufactured by the chlorination of camphenes, whereas strobane results from the chlorination of a mixture of camphenes and pinenes. For the calculation of toxaphene:

- Adjust the sample size so that the major toxaphene peaks are 10-70% of full scale.
- Inject a toxaphene standard that is estimated to be within 10 ng of the sample amount.
- Quantitate using the 5 major peaks or the total area of the toxaphene pattern:

To measure total area, construct the baseline of standard toxaphene between its extremities and construct the baseline under the sample peaks, using the distances of the peak troughs to baseline on the standard as a guide. The relative heights and widths of the peaks in the sample may not be identical to the standard.

A series of toxaphene residues have been calculated using the total peak area for comparison to the standard and also using the area of the last 4 peaks only, in both sample and standard. The agreement between the results obtained by the 2 methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram shows interferences from other substances such as DDT.

A.2 **Chlordane** - Chlordane is a technical mixture of at least 11 major and 30 minor components. *Trans*- and *cis*-chlordane ($\alpha$ and $\gamma$, respectively), are the 2 major components of chlordane. The exact percentage of each component is not consistent from batch to batch.

The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factor such as water and sunlight.

Whenever possible, when a chlordane residue does not resemble chlordane, the analyst should quantitate the peaks of $\alpha$-chlordane, $\gamma$-chlordane, and heptachlor separately against the appropriate reference materials, and report the individual results.

When the GC pattern of the residue resembles that of technical chlordane, the analyst may quantitate chlordane residues by comparing the total area of the chlordane chromatogram using the 5 major peaks or the total area. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected chlordane area.

To measure the total area of the chlordane chromatogram, inject an amount of a technical chlordane standard which will produce a chromatogram in which the major peaks are approximately the same size as those in the sample chromatograms.

**Note:** Octachloro epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.

A.3 **Hexachlorocyclohexane** - Hexachlorocyclohexane consists of a mixure of 6 chemically distinct isomers of benzene hexachloride (BHC) and one or more heptachloro- and octachloro-cyclohexanes. Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. Quantitate each isomer ($\alpha$, $\beta$, $\gamma$, and $\delta$) separately against a standard of the respective pure isomer.

A.4 **DDT** - Technical DDT consists primarily of a mixture of 4,4'-DDT (~75%) and 2,4'-DDT (~25%). As DDT weathers, 4,4'-DDE, 2,4'-DDE, 4,4'-DDD, and 2,4'-DDD are formed. Since the 4,4'- isomers of DDT, DDE, and DDD predominate in the environment, these are the isomers normally regulated by the EPA. Sample extracts should be quantitated against standards of the respective pure isomers of 4,4'-DDT, 4-4'-DDE, and 4,4'-DDD.

# DATA REVIEW

| | | YES | NO | CA | FLAG |
|---|---|---|---|---|---|
| 1 | Check standard recoveries within ± 15 % ? | | | | |
| (8081) 1b | Prime and blank run? | | | | |
| (8081) 1c | Endrine DDT breakdown < 15 % ? | | | | |
| (8270) 1d | DFTPP tune evaluated and passing? | | | | |
| (8270) 1e | SPCC average response factor > 0.050 ? | | | | |
| (8270) 1f | CCC % deviation > 20 % ? | | | | |
| (8270) 1g | Internal recoveries within 50-100 % ? | | | | |
| 2 | Method blank recoveries < reporting limits? | | | | |
| 3 | LCS within control limits? | | | | |
| 4 | MS/MSD within control limits? | | | | |
| 5 | All surrogate recoveries within control limits? | | | | |
| 6 | All hits out of cal range diluted and re-analyzed? | | | | |
| 7 | All sample holding times met? | | | | |
| 8 | No transcription errors? | | | | |
| 9 | No calculation errors? | | | | |

COMMENTS:

Analyst review signature: _____ Date: _____

# Method Detection Limits (MDL), Practical Quantitation Limits (PQL), and Reporting Limits (RL)

**Method: Pesticides by 8081**

| Analyte | Water (µg/L) | | | Soil (µg/Kg) | | |
|---|---|---|---|---|---|---|
| | MDL | PQL | RL | MDL | PQL | RL |
| alpha-BHC | 0.0034 | 0.012 | 0.025 | 0.073 | 0.26 | 0.25 |
| gamma-BHC | 0.0023 | 0.008 | 0.025 | 0.077 | 0.27 | 1 |
| beta-BHC | 0.0033 | 0.012 | 0.025 | 0.121 | 0.43 | 1 |
| Heptachlor | 0.0037 | 0.013 | 0.025 | 0.051 | 0.18 | 1 |
| delta-BHC | 0.0018 | 0.007 | 0.025 | 0.082 | 0.29 | 1 |
| Aldrin | 0.0046 | 0.016 | 0.025 | 0.150 | 0.53 | 1 |
| Heptachlor epoxide | 0.0018 | 0.007 | 0.025 | 0.053 | 0.19 | 1 |
| Endosulfan 1 | 0.0087 | 0.031 | 0.05 | 0.137 | 0.49 | 1 |
| 4,4-DDE | 0.0032 | 0.011 | 0.025 | 0.057 | 0.20 | 2 |
| Dieldrin | 0.0026 | 0.009 | 0.01 | 0.046 | 0.16 | 2 |
| Endrin | 0.0011 | 0.004 | 0.05 | 0.060 | 0.21 | 2 |
| 4,4-DDD | 0.0048 | 0.017 | 0.05 | 0.133 | 0.47 | 2 |
| Endosulfan 11 | 0.0017 | 0.006 | 0.05 | 0.103 | 0.36 | 2 |
| 4,4-DDT | 0.0040 | 0.014 | 0.05 | 0.095 | 0.34 | 2 |
| Endrin aldehyde | 0.0027 | 0.010 | 0.05 | 0.055 | 0.19 | 2 |
| Endosulfan sulfate | 0.0052 | 0.018 | 0.05 | 0.134 | 0.48 | 2 |
| Methoxychlor | 0.0130 | 0.046 | 0.5 | 0.863 | 3.06 | 20 |
| Chlordane (*) | 0.1 | N/A | 0.5 | 3.33 | N/A | 20 |
| Toxaphene (*) | 0.5 | N/A | 2 | 16.6 | N/A | 80 |

(*)--This compound is a multi-component analyte. The MDL for this analyte is based on the lowest concentration at which pattern recognition can be performed.

Copy #: 1312-_____

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## SYNTHETIC PRECIPITATION LEACHING PROCEDURE (SPLP)

## GLA 1312 BG

Revision 1.0

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for performing the synthetic precipitation leaching procedure (SPLP). This SOP is an interpretation of EPA Method SW-846 no. 1312. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

## 1.1 MATRICES

This method is applicable to liquid, solid, and multi-phasic samples.

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

The synthetic precipitation leaching procedure (SPLP) is designed to simulate the leaching wastes will undergo when exposed to rain water. Samples are extracted with sulfuric acid/nitric acid solution at pH 4.2 or 5.0 (water for samples that may contain cyanide and for analysis of volatile compounds) for 18 ± 2 hours. The specific extraction fluid used depends upon the source of the sample (east or west of the Mississippi River). This SPLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multi-phasic samples.

2.1 Liquid samples (*i.e.* samples containing less than 0.5% dry solid material) are filtered through a 0.6 to 0.8 µm glass fiber filter to produce the SPLP extract.

2.2 For samples containing more than 0.5% solids, the liquid (if any) is separated from the solid phase and stored for later analysis. The particle size of the solid phase is reduced if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the sample. Zero-headspace extractors (ZHE) are used when testing for volatile analytes. (See Appendix A for a list of volatile compounds.) Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 - 0.8 µm glass fiber filter.

2.3 If compatible (*i.e.* multiple phases will not form on combination), the initial liquid phase of the sample is added to the liquid extract, and analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

## 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

### 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous components. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

## 4.0 INTERFERENCES

4.1 Potential interferences that may be encountered during analyses are discussed in the individual analytical methods.

4.2 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly. Periodic cleaning of sample preparation and analysis areas will be performed. Deionized water used for the extraction of volatile analytes must be boiled for a minimum of one hour prior to use to remove low level contaminants.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all SPLP extractions performed.

5.2 SPLP Logbooks:

Logbooks will be maintained for all SPLP extractions. Examples of sheets for these logbooks can be found in Appendix B. All information regarding samples processed in the lab will be entered into these books. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Analyst's signature and date/times of extraction
- All readings, including volumes and weights of materials
- Sample matrix type
- Final extraction volume and pH
- Initial sample weight used
- LCS and matrix spike information

This logs should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

## 6.0 QUALITY CONTROL

### 6.1 METHOD BLANK

A minimum of 1 blank (using the same extraction fluid and vessel type as the samples) must be analyzed for every batch of extractions that have been conducted in an extraction vessel. Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks should produce a concentration below the reporting limit (e.g. PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

### 6.2 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

## 7.0 SAMPLE MANAGEMENT

**7.1** The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

**7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "SPLP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

### 8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

## 9.0 EQUIPMENT

9.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessels in an end-over-end fashion at 30 ± 2 rpm (see Figure 1). The rotation rate of each device should be checked monthly by placing a highly-visible marker on the device and counting the number of revolutions over a 60 second period. Some examples of suitable apparatus are: Analytical Testing & Consulting Services no's. DC20x and DC24C, Associated Design & Manufacturing Company no's. 3740-nn-BRE, Environmental Machine & Design no. 08-00-00, IRA Machine Shop & Laboratory no. 011011, Lars Lande Manufacturing no. 10VRE, and Millipore Corp. no's.4-ZHE and YT310RAHW.

9.2 Zero-headspace extraction vessels (ZHE): These devices are only used when the sample is being tested for the mobility of volatile analytes. The ZHE (see Figure 2) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel. The vessels have an internal volume of 500-600 mL, and are equipped to accommodate a 90-110 mm filter. The devices contain VITON o-rings which should be replaced when worn. Some examples of suitable ZHE devices are: Analytical Testing & Consulting Services no. C102, Associated Design & Manufacturing Company no. 3745-ZHE, Environmental Machine & Design no. VOLA-TOX1, Lars Lande Manufacturing no. ZHE-11, and Millipore Corp. YT30090HW.

- The components of the ZHE extractors which will contact the samples (expecially the viton rubber components) should be heated in a 105°C oven for a period of one hour and allowed to cool completely before assembling the extractors.
- For the ZHE to be acceptable for use, the piston within the device should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the o-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for SPLP analyses and the device repaired or discarded.
- The ZHE devices should be checked for leaks after each extraction. If the devices contain built-in pressure gauges, pressurize to 50 psi, allow to stand for 1 hour, and recheck the pressures. If the devices do not have built-in pressure meters, pressurize to 50 psi, submerge in water, and check for air bubbles escaping from any of the fittings. If pressure is lost, check all fittings, inspect (and replace if necessary) the o-rings, and then retest the device. If leakage problems cannot be solved, the device cannot be used.
- Some ZHE devices use gas pressure to actuate the ZHE piston, while others use mechanical pressure. Whereas the volatiles SPLP procedure refers to pressure in psi, the pressures applied to mechanically actuated pistons are measured in torque (inch-pounds). *Refer to the manufacturer's instructions for the proper conversion from psi to inch-lbs.*

9.3 Bottle extraction vessels: When sample is being evaluated for non-volatile analytes, bottles with sufficient capacity to hold samples and appropriate volumes of extraction fluid are needed. (Headspace is allowed for non-volatile SPLP.)
The extraction bottles may be constructed from various materials, depending upon the analytes to be analyzed, and the nature of the sample. Polytetrafluoroethylene (PTFE, Teflon) plastic or fluorinated HDPE bottles must be used if organics are to be investigated. Borosilicate glass bottles should be used instead of other types of glass bottles when inorganics are of concern. Bottles may come from the manufacturer washed and ready for metal analyses. Some examples of suitable bottles are: Eagle-Picher 500-mL and 2-L natural HDPE wide mouth jars with PP lids - level 1 - no's. 151-500W/WM and 150-02W/WM, and Nalge 2-L fluorinated (FLPE) bottles no. 2097-0005.

9.4 Filtration devices: Filtrations should be performed in a hood. When the sample is to be evaluated for volatile components, the ZHE vessel is used for filtration. (Note: If it is suspected that the glass fiber filter has ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.) Otherwise, any filter holder capable of supporting a glass fiber filter and withstanding the pressure required for separations may be used. These devices should have a minimum internal volume of 300 mL and accommodate a minimum filter size of 47 mm - devices capable of 1.5 L volume using 142 mm diameter filters are recommended. Vacuum filtration can only be used for samples with low solids content (*e.g.* < 10%), and for highly granular, liquid-containing samples. All other types of samples should be filtered using positive pressure filtration. Some examples of suitable filter holders are: Micro Filtration Systems no. 302400, Millipore Corp. no. YT30142HW, and Nucleopore Corp. no. 425910. (Note: Extraction vessels and filtration devices must be made of inert materials which will not leach or absorb sample components. Glass, PTFE, and stainless steel 316 equipment may be used for organic and inorganic component analyses. High density polyethylene - HDPE, polypropylene - PP, and polyvinyl chloride - PVC - equipment may be used for metals.)

9.5 Filters: Borosilicate glass fiber, without binder materials, effective pore size 0.6 to 0.8 µm. Acid-washed filters (1 N nitric acid followed by reagent water, or purchased) must be used for metal analyses. Glass fiber filters are fragile and should be handled with care. Some examples of suitable filters are: Gelman Science no. 66257, Micro Filtration Systems GF75, Millipore Corp. no. AP40, Nucleopore Corp. no. 211625, and Whatman no. GFF, acid-washed 1810-142.

9.6 ZHE extract collection devices: TEDLAR® bags are used to collect the initial liquid phase and the final extract using ZHE devices.

- If the sample contains an aqueous liquid phase or if a sample does not contain a significant amount of non-aqueous liquid (*i.e.* < 1% of total), the TEDLAR bag or a 600-mL syringe may be used to collect and combine the initial liquid and solid extract.
- If a sample contains a significant amount of non-aqueous liquid in the initial liquid phase (*i.e.* > 1% of total), the syringe or the TEDLAR bag may be used for both the initial liquid/solid separation and the final extract filtration. However, analysts should use one or the other, not both.
- If the sample contains no initial liquid phase (*i.e.* 100% solids) or has no significant solid phase (*i.e.* 100% liquid), either a TEDLAR bag or a syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

9.7 ZHE extraction fluid transfer device: Any device capable of transferring extraction fluid into the ZHE devices without changing the nature of the extraction fluid (*e.g.* positive displacement or peristaltic pump, gas-tight syringe, pressure filtration unit).

9.8 Laboratory balance, calibrated, capable of weighing up to 1 kg (?) with 0.01 g accuracy (all weight measurements are to be within ± 0.1 g).

9.9 pH Meter and probe - standardized and accurate to ± 0.05 units at 25°C.

9.10 Thermometer, capable of storing minimum and maximum temperatures over the range of 15-30°C (Fisher no. 15-077-17B, or equivalent).

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water) - no interferants at or above the detection limits for the methods. Reagent water for volatile extractions may be prepared passing DI water through a carbon filter, using a Millipore Super-Q system (or equivalent), and boiling for one hour.

10.2 Nitric acid - concentrated $HNO_3$, ACS/reagent grade, **CAUTION:** Nitric acid is corrosive.

10.3 Sulfuric acid - concentrated $H_2SO_4$, ACS/analytical reagent grade, **CAUTION:** Sulfuric acid is corrosive.

10.4 Sulfuric acid/nitric acid (60/40 wt% mixture): Cautiously mix 6.0 g of concentrated $H_2SO_4$ with 4.0 g of concentrated $HNO_3$ and dilute to 250ml with reagent water.

10.5 Extraction Fluid #1 (for samples obtained from sites east of the Mississippi River): For each liter of extraction fluid, add sulfuric acid/nitric acid mixture into 1 L of reagent water until the pH is 4.20 ± 0.05.

10.6 Extraction Fluid #2 (for samples obtained from sites west of the Mississippi River): For each liter of extraction fluid, add sulfuric acid/nitric acid mixture into 1 L of reagent water until the pH is 5.00 ± 0.05.

10.7 Extraction Fluid #3 (for cyanide and volatiles leachability): Use reagent water.

**NOTE:** Solutions are unbuffered and exact pH may not be attained.

**NOTE:** Extraction fluids should be monitored for impurities. The pH should be checked prior to use to ensure that they were prepared correctly. If impurities are found, or the pH is not within specifications, the fluid is discarded and fresh extraction fluid prepared. Also see Appendix B for example of logsheet for preparation of extraction fluids.

## 11.0 PROCEDURE

**NOTE:** Record all pertinent sample information in the logbooks. See Appendix C for guidelines for sample collection, preservation, and handling.

### 11.1 PRELIMINARY EVALUATIONS

Preliminary SPLP evaluations may be performed on a minimum 100 g aliquot of sample. This aliquot may not actually undergo SPLP extraction. These preliminary evaluations may include:

- determination of the percent solids (section 11.1.1);
- determination of whether the sample contains insignificant solids and therefore can be used directly for analyses, following filtration (section 11.1.2);
- determination of whether the solid portion of the sample requires particle size reduction (section 11.1.3); and
- determination of appropriate extraction fluid (section 11.1.4).

11.1.1 DETERMINATION OF PERCENT SOLIDS: Percent solids is defined as that fraction of a sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below:

- If the sample will obviously yield no liquid when subjected to pressure filtration (*i.e.* is 100% solids), proceed to section 11.1.3.
- If the sample is liquid or multi-phasic, separation of the liquid phase from the solid phase is required:
  - Pre-weigh the filter and the container that will receive the filtrate.
  - Assemble the filter holder and filter. Place the filter on the support screen and secure.
  - Weigh a subsample (100 g minimum) and record the weight.
  - Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the sample through the same filtration system.
  - Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of cold sample (from refrigerator) reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.
  - Gradually apply vacuum or gentle pressure (1-10 psi) until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved though the filter, and if no additional liquid has passed through the filter in any 2 minute period, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (*i.e.* filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.
  - The material in the filter holder is defined as the solid portion of the sample, and the filtrate is the liquid phase.
  - Determine the weight of the liquid phase by subtracting the weight of the filtrate container from the weight of the filtrate container from the total weight of the filtrate-filled container. Determine the weight of the solid phase by subtracting the weight of the liquid phase from the weight of the total sample used.
  - Record the weights of the liquid and solid phases. Calculate the percent solids:

$$\textit{Percent solids (\%)} = \frac{\textit{Weight of solid}}{\textit{Total weight of sample}} \times 100$$

**NOTE:** If sample material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the total sample weight for the actual amount of the sample that will be filtered.

**NOTE:** Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

**NOTE:** Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material within the filtration device is considered as being solid. Do not replace the original filter with a fresh filter under any circumstances - use only one filter.

11.1.2 NON-SOLID SAMPLES: If the percent solids is less than 0.5%, then proceed to section 11.2.9 if the non-volatile SPLP is to be performed, and/or to section 11.3 (with a fresh portion of the sample) if the volatile SPLP is to be performed. If the percent solids is equal to or greater than 0.5%, then proceed to section 11.1.3 to determine whether the solid material requires particle size reduction, or perform the procedure outlined below if it is noticed that a small amount of the filtrate is entrained in wetting of the filter:

- Remove the solid phase and filter from the filtration apparatus.
- Dry the filter and solid phase at 100 ± 20°C until 2 successive weighings yield the same value within ± 1%. Record the final weight.
- Calculate the percent dry solids:

$$\text{Percent dry solids (\%)} = \frac{(\text{Weight of dry sample + filter}) - \text{Tared weight of filter}}{\text{Initial weight of sample}} \times 100$$

- If the percent dry solids is less than 0.5%, then proceed to section 11.2.9 if the non-volatile SPLP is to be performed, and/or to section 11.3 if the volatile SPLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the non-volatile SPLP is to be performed, return to the beginning of this section (11.1), and with a fresh portion of sample, determine whether particle size reduction is necessary (section 11.1.3).

**NOTE:** Caution should be taken to ensure that the subject solid will not flash or react violently upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

11.1.3 PARTICLE SIZE REDUCTION: Using the solid portion of the sample, evaluate the solid for particle size. Particle size reduction is required unless the solid has a surface area per gram of material equal to or greater than 3.1 $cm^2$, or is smaller than 1 cm in its narrowest dimension (*i.e.* capable of passing through a 9.5 mm - 0.375 inch - standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the sample to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see section 11.3.6).

**NOTE:** Surface area criteria are meant for filamentous (*e.g.* paper, cloth, and similar) materials. Actual measurement of surface area is not required, nor is recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is not currently available.

11.1.4 DETERMINATION OF APPROPRIATE EXTRACTION FLUID:

For wastes and wastewater, use extraction fluid #1.

For soils, if the sample is from a site that is east of the Mississippi River, use extraction fluid #1; if the site is west of the Mississippi River, use extraction fluid #2.

For cyanide-containing wastes and/or soils, extraction fluid #3 (water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

11.1.5 If the aliquot of the sample used for the preliminary evaluation (sections 11.1.1 - 11.1.4) was determined to be 100% solid, then it can be used for the section 11.2 extraction (assuming at least 100 g remain), and the section 11.3 extraction (assuming at least 25 g remain). If the aliquot was subjected to the filtration procedure described in section 11.1.1, then another aliquot is used for the volatile procedure in section 11.3. The aliquot of the sample subjected to the filtration procedure in 11.1.1 might be appropriate for the section 11.2 extraction if an adequate amount of solid was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to section 11.2.10 of the non-volatile SPLP.

## 11.2 SPLP PROCEDURE FOR NON-VOLATILE ANALYTES

A minimum sample size of 100 g (liquid and solid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the sample, whether the initial liquid phase of the sample will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of SPLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single SPLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed, and the extracts from each combined and aliquoted for analysis.

11.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (*i.e.* is 100% solid), weigh a subsample (100 g minimum) and proceed to section 11.2.3.

11.2.2 If the sample is liquid or multi-phasic, liquid/solid separation is required.

- Pre-weigh the container that will receive the filtrate.
- Assemble the filter holder and filter. Place the filter on the support screen and secure. (Filters must be acid-washed for analysis of metals - acid-washed filters may be used for all non-volatile extractions, even when metals are not of concern.)
- Weigh a subsample (100 g minimum) and record the weight. If the sample contains less than 0.5% dry solids, the liquid portion of the sample, after filtration, is the SPLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required. For samples containing more than 0.5% dry solids, use the percent solids information to determined the optimum sample size (100 g minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the SPLP extract.
- Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the sample is centrifuged, the liquid should be decanted and filtered, followed by filtration of the solid portion of the sample through the same filtration system.
- Quantitatively transfer the sample (liquid and solid phases) to the filter holder. Spread the sample evenly overt the surface of the filter. If filtration of cold sample (from refrigerator) reduces the amount of expressed liquid compared to what would be expressed at room temperature, then allow the sample to warm to room temperature in the device before filtering.

- Gradually apply vacuum or gentle pressure (1-10 psi) until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved though the filter, and if no additional liquid has passed through the filter in any 2 minute period, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (*i.e.* filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.
- The material in the filter holder is defined as the solid phase of the sample, and the filtrate is the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (see Section 11.2.6) or stored refrigerated until time of analysis.

**NOTE:** *If sample material (>1% of original sample weight) has obviously adhered to the* container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the total sample weight for the actual amount of the sample that will be filtered.

**NOTE:** Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

**NOTE:** Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, this material may not filter. If this is the case, the material within the filtration device is considered as being solid. Do not replace the original filter with a fresh filter under any circumstances - use only one filter.

11.2.3 If the sample contains less than 0.5% dry solids (section 11.1.2), proceed to section 11.2.7. If the sample contains greater than 0.5% dry solids (see section 11.1.1 or 11.1.2), and if particle size reduction of the solid was needed (section 7.1.3), proceed to section 11.2.4. If the sample, as received, passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to section 11.2.5.

11.2.4 Prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the sample to a surface area of particle size as described in section 11.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

**NOTE:** Sieving of the sample is not normally required. Surface area requirements are meant for filamentous (*e.g.* paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

11.2.5 Determine the amount of extraction fluid to add to the extractor vessel:

$$\textit{Weight of extraction fluid} = \frac{20 \times \textit{percent solids (11.1.1)} \times \textit{weight of sample filtered (11.2.2)}}{100}$$

Slowly add the appropriate extraction fluid (section 11.1.4) to the extractor vessel. Close the extractor bottle tightly (Teflon tape can be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Monitor the ambient temperature (room temperature) using a min/max thermometer (be sure to reset at start of extraction time). Ambient temperature should be maintained at 23 ± 2°C during the extraction period.

**NOTE:** As agitation continues, pressure may build up within the extractor bottle for some types of samples (*e.g.* limed or calcium carbonate containing sample may evolve gases such as carbon dioxide). The extractor bottle may be periodically opened (*e.g.* after 15 minutes, 30 minutes, and 1 hour) and vented into a hood to relieve excess pressure.

11.2.6 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in section 11.2.2. For final filtration of the SPLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Acid-washed filters are used if evaluating the mobility of metals.

11.2.7 Prepare the SPLP extract:

- If the sample contained no initial liquid phase, the filtered material obtained from section 11.2.6 is the SPLP extract. Proceed to section 11.2.8.
- If compatible (*e.g.* multiple phases will not result on combination), combine the filtered liquid resulting from section 11.2.6 with the initial liquid phase of the sample obtained in section 11.2.2. This combined liquid is the SPLP extract. Proceed to section 11.2.8.
- If the initial liquid phase of the sample is not, or may not be, compatible with the filtered liquid resulting from section 11.2.2, do not combine these liquids. Analysis the liquids separately, and combine the results as the SPLP extract.

11.2.8 Following collection of the SPLP extract, the pH of the extract is determined and recorded. Immediately aliquot and preserve the extracts for analysis. Aliquots for metals must be acidified with nitric acid to a pH of less than 2. If precipitation is observed upon addition of nitric acid to a small amount of the extract, then the remaining portion of the extract for metals analysis is not acidified, and the extract analyzed as soon as possible. All other aliquots must be stored under refrigeration until analyzed. The SPLP extracts will be prepared and analyzed according to the appropriate analytical methods. SPLP extracts to be analyzed for metals will be acid digested, except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the sample is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the sample is not hazardous. If individual phases are analyzed separately, determine and record the volume of the individual phases (to ± 0.5%).

## 11.3 SPLP PROCEDURE FOR VOLATILE ANALYTES

Zero-headspace extraction (ZHE) devices are used to obtain SPLP extracts for analysis of volatile compounds only. Extracts resulting from the use of the ZHE are not used to evaluate the mobility of non-volatile analytes (e.g. metals and pesticides).

- The ZHE device has a capacity of approximately 500 mL. The ZHE can accommodate a maximum of 25 g of solid due to the requirement to add an amount of extraction fluid equal to 20 times the weight of the solid phase.
- Charge the ZHE with sample only once, and do not open the device until the final extract has been collected. Repeated filling of the ZHE to obtain 25 g of solid is not permitted.
- Do not allow the sample, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (~4°C) to minimize loss of volatile components.
- One of the ZHE devices in each analytical batch is used for the blank. Sequence through the devices such that each will be used for the blank.

11.3.1 Pre-weigh the (evacuated) filtrate collection container and set aside. If using a TEDLAR bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis.

11.3.2 Place the ZHE piston within the body of the ZHE (it may be helpful to first moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements).

11.3.3 If the sample is 100% solids, weigh a subsample (25 g maximum), record weight, and proceed to section 11.3.5.

11.3.4 If the sample contains less than 0.5% dry solids, the liquid portion of sample, after filtration, is the SPLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For samples containing more than 0.5% dry solids, use the percent solids information (section 11.1.1) to determine the optimum sample size to charge into the ZHE. The recommended sample size is:

- For samples containing less than 5% solids, weigh a 500 g subsample and record the weight.
- For samples containing greater than 5% solids, determine the amount of sample to charge into the ZHE: *Weight (g) = 25g / (percent solids result, as a decimal)*. Weigh a subsample of the appropriate size and record the weight.

11.3.5 If particle size reduction of the solid portion of the sample is not required, proceed to section 11.3.7. Otherwise continue with section 11.3.6.

11.3.6 Prepare the sample for extraction by crushing, cutting, or grinding the solid portion of the sample to an acceptable surface area or particle size (see section 11.1.3). Samples and appropriate reduction equipment should be refrigerated, if possible, prior to particle size reduction. The means used to effect particle size reduction must not generate heat in and of itself. If reduction of the solid phase of the sample is necessary, exposure of the sample to the atmosphere should be avoided to the highest extent possible.

**NOTE:** Sieving of the sample is not recommended due to the possibility that volatile components may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (*e.g.* paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

11.3.7 The solid phase of sample slurries does not have to settle. Do not centrifuge samples prior to filtration.

11.3.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

**NOTE:** If sample material (greater than 1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in section 11.3.4 to determine the weight of the sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1-10 psi (or more if necessary) to force all headspace slowly out of the ZHE device (into a hood). At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of cold sample (from refrigerator) reduces the amount of expressed liquid over what would be expected and room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the sample is 100% solid, slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device, and proceed to section 11.3.12.

11.3.9 Attach the evacuated tedlar bag to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1-10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed though the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate in any 2 minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, disconnect and weigh the filtrate collection container.

**NOTE:** Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

11.3.10 The material in the ZHE is the solid phase of the sample and the filtrate is the liquid phase.

**NOTE:** Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the SPLP extraction as a solid.

If the original sample contained less than 0.5% dry solids (see section 11.1.2), this filtrate is the SPLP extract and is analyzed directly. Proceed to section 11.3.15.

11.3.11 The liquid phase may now be analyzed immediately (see sections 11.3.13 - 11.3.15) or stored under refrigeration and with minimal headspace until time of analysis. Determine the weight of extraction fluid #3 to add to the ZHE:
*Weight = 20 × (percent solids) × (weight of sample filtered) / 100*

11.3.12 The following details how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #3 (reagent water) is used in all cases.

- With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (form the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.
- After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5-10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding should be done quickly and be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5-10 psi and check all ZHE fittings to ensure that they are closed.
- Place the ZHE in a rotary agitation apparatus and rotate at 30 ± 2 rpm for 18 ± 2 hours. Monitor the ambient temperature (room temperature) using a min/max thermometer (be sure to reset at start of extraction time). Ambient temperature should be maintained at 23 ± 2°C during the extraction period.

11.3.13 Following the 18 ± 2 hour agitation period, check the pressure behind the ZHE piston by reading the gauge and quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (*i.e.* no gas release observed), check the ZHE for leaking, and extract a fresh portion of sample (using another ZHE if necessary). If the pressure within the device has been maintained, the material in the extractor is separated into its component liquid and solid phases. If the sample contained an initial liquid phase, the liquid may be filtered directly into the same filtrate container holding the initial liquid phase. A separate filtrate collection container must be used if combining the liquids would create multiple phases, or these is not enough empty volume remaining within the initial filtrate collection container. Filter through a glass fiber filter using the ZHE device, as described in section 11.3.9. All extract is filtered and collected if a TEDLAR bag is used, if the extract is multi-phasic, or if the sample contained an initial liquid phase (see section 11.3.1).

**NOTE:** If it is suspected that the glass fiber filter has ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

11.3.14 If the original sample contained no initial liquid phase, the filtered liquid material from section 11.3.13 is the SPLP extract. If the sample contained an initial liquid phase, the initial liquid phase (section 11.3.9) and the filtered liquid material (11.3.13) are collectively the SPLP extract.

11.3.15 Following collection of the SPLP extracts, immediately prepare the extracts for analysis and store refrigerated with minimal headspace until time of analysis. The SPLP extracts are analyzed according to the appropriate analytical methods. If individual phases are analyzed separately, determine and record the volume of the individual phases (to ± 0.5%).

### 11.4 ANALYTICAL RESULTS

If the individual phases were analyzed separately (*e.g.* they are not miscible), mathematically combine the results using a simple volume-weighted average:

$$\textit{Final analyte concentration} = \frac{V_1 \times C_1 + V_2 \times C_2}{V_1 + V_2}$$

where:
$V_1$ = volume of the first phase (in L);
$C_1$ = concentration of the analyte of concern in the first phase (mg/L);
$V_2$ = volume of the second phase (in L); and
$C_2$ = concentration of the analyte of concern in the second phase (mg/L).

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 13.0 REFERENCES

13.1 Method SW-846, 1312: Synthetic Precipitation Leaching Procedure.
13.2 Great Lakes Analytical Quality Assurance Program.
13.3 Great Lakes Analytical Chemical Hygiene Plan.
13.4 Great Lakes Analytical SOP for Login Department.
13.5 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

Refer to Great Lakes Analytical Quality Assurance Program Manual.

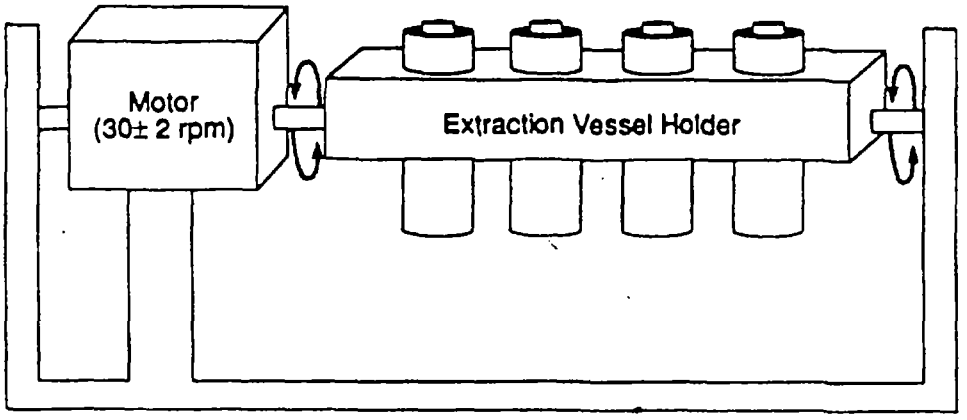



Figure 1. Rotary Agitation Apparatus

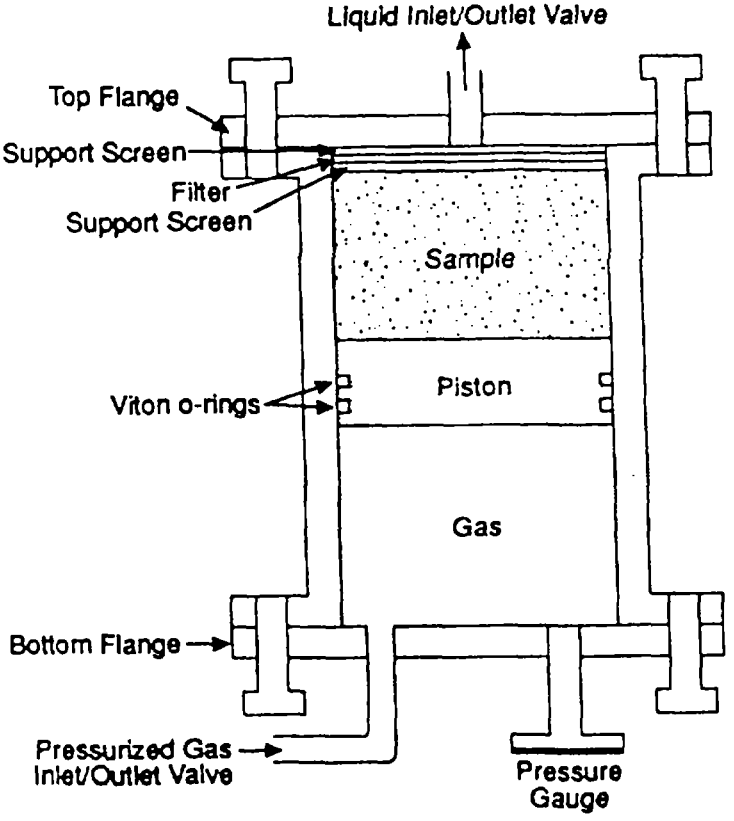



Figure 2. Zero-Headspace Extractor (ZHE)

# APPENDIX A.

## SPLP VOLATILE ANALYTES.

*The zero-headspace extractor vessel must be used when testing for any or all of these analytes:*

| | |
|---|---|
| Acetone | |
| Benzene | @ |
| n-Butyl alcohol | |
| Carbon disulfide | |
| Carbon tetrachloride | @ |
| Chlorobenzene | @ |
| Chloroform | @ |
| 1,2-Dichloroethane | @ |
| 1,1-Dichloroethylene | @ |
| Ethyl acetate | |
| Ethyl benzene | |
| Ethyl ether | |
| Isobutanol | |
| Methanol | |
| Methylene chloride | |
| Methyl ethyl ketone | @ |
| Methyl isobutyl ketone | |
| Tetrachloroethylene | @ |
| Toluene | |
| 1,1,1-Trichloroethane | |
| Trichlorofluoromethane | |
| 1,1,2-Trichloro-1,2,2-trifluoroethane | |
| Vinyl chloride | @ |
| Xylene | |

@ = Toxicity characteristic constituent.

# APPENDIX B.

# EXAMPLES OF SPLP LOGBOOK SHEETS.

B.1 Extraction Fluid Preparation and Testing Log.

B.2 Solids Extraction Preparation.

B.3 Multi-Phase and Liquid Sample Preparation.

B.4 ZHE Extraction for SPLP Volatiles.

B.5 Extraction Device Rotation Speed.

**Appendix B1.**

## SYNTHETIC PRECIPITATION LEACHING PROCEDURE LOGSHEET

### EXTRACTION FLUID PREPARATION AND TESTING LOG

| PREPARE FRESH FLUID(S) AS FOLLOWS: | |
|---|---|
| Fluid #1: | For each liter of extraction fluid, add sulfuric acid/nitric acid mixture into 1 L of reagent water until the pH is 4.20 ± 0.05. |
| Fluid #2 | For each liter of extraction fluid, add sulfuric acid/nitric acid mixture into 1 L of reagent water until the pH is 5.00 ± 0.05. |
| Fluid #3 | Use reagent water. |

| Date | New Prep. or Test of Prev. ? | Fluid Type (#1 or #2) | Volume Prepared (L) | Sulfuric Acid-Nitric Acid Mixture Reference | pH | Initials |
|---|---|---|---|---|---|---|
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**Appendix B2.**

| SYNTHETIC PRECIPITATION LEACHING PROCEDURE LOGSHEET | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| SOLIDS EXTRACTION PREPARATION | | | | | | | | | | |
| **Great Lakes Analytical** | | | | | | **Date:** | | | | |
| ***GLA Sample I.D.:*** | | | | | | | | | | |
| **A. Sample Description** | | | | | | | | | | |
| 1. Solid only | | | | | | | | | | |
| **B. Percent Solid Phase** | | | | | | | | | | |
| 1. Check if 100% solids | | | | | | | | | | |
| **C. Selection of Extraction Fluid (Does not apply to volatile organic components.)** | | | | | | | | | | |
| 1. Particle size reduced? y/n | | | | | | | | | | |
| 2. If sample is from a site east of Mississippi River, check box, use extraction fluid #1 | | | | | | | | | | |
| 3. If sample is from a site west of Mississippi River, check box, use extraction fluid #2 | | | | | | | | | | |
| 4. If sample may contain cyanide or is waste or wastewater, check box, use extrctn fluid #3 | | | | | | | | | | |
| **D. Sample Size for Leachables Testing** | | | | | | | | | | |
| 1. Check if 100 g sample used, or enter actual weight | | | | | | | | | | |
| **E. Determination of Amount of Extraction Fluid Used** | | | | | | | | | | |
| 1. 20 × sample weight | | | | | | | | | | |
| **F. Record of Extraction Data** | | | | | | Analyst's signature | | | Date | |
| 1. Extraction start time | | | | AM / PM | | | | | | |
| 2. Extraction stop time | | | | AM / PM | | | | | | |
| 3. Min. ambient temperature | | | | °C | | | | | | |
| 4. Max. ambient temperature | | | | °C | | | | | | |
| 5. *pH of filtrate* | | | | | | | | | | |
| 6. Volume of filtrate (mL) | | | | | | | | | | |

Appendix B3.

| SYNTHETIC PRECIPITATION LEACHING PROCEDURE LOGSHEET | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| MULTI-PHASE AND LIQUID EXTRACTION PREPARATION | | | | | | | | | | |
| **Great Lakes Analytical** | | | | | | **Date:** | | | | |
| **GLA Sample I.D.:** | | | | | | | | | | |
| **A. Sample Description - check appropriate boxes** | | | | | | | | | | |
| 1. Solids | | | | | | | | | | |
| 2. Liquid(s) | | | | | | | | | | |
| a. Aqueous liquid (water) | | | | | | | | | | |
| b. Non-aqueous liquid | | | | | | | | | | |
| **B. Percent Solid Phase Determination** | | | | | | | | | | |
| 1. Weight of filter (g) | | | | | | | | | | |
| 2. Weight of subsample (100 g) | | | | | | | | | | |
| 3. Weight of filter container (g) | | | | | | | | | | |
| 4. Weight of filter container and filtrate (g) | | | | | | | | | | |
| 5. Weight of filtrate (g): *(B.4 - B.3)* | | | | | | | | | | |
| 6. Weight percent solids (wet): *(B.2 - B.5) / B.2 x 100* | | | | | | | | | | |
| 7. Weight of *dried* solids and filter (g) | | | | | | | | | | |
| 8. Weight percent solids (dry): *(B.7 - B.1) / B.2 x 100* | | | | | | | | | | |
| 9. Volume of initial aqueous filtrate (as applicable) | | | | | | | | | | |
| 10. Volume of initial organic filtrate (as applicable) | | | | | | | | | | |
| **C. Determination of Sample Weight Required to Support All Analyses** | | | | | | | | | | |
| NOTE: If percent solids (determined above) ≥ 75%, use 100 g, and proceed with extraction procedure. | | | | | | | | | | |
| 1. M - Metals analyses: enter 3 for Hg, 1 for no Hg | | | | | | | | | | |
| 2. SV - No. of semi-volatile analyses: 8270, 8150, 8080 (1-3) | | | | | | | | | | |
| 3. QC - Is QC to be run on this sample? (no=1, yes=3) | | | | | | | | | | |
| 4. Calculate the original sample weight required for each sample: *Original sample weight (g) = (0.011) x QC x [(M x 50) + (SV x 100)] / 20 / (percent solids)* | | | | | | | | | | |
| 5. Calculated sample weight to be filtered prior to extraction | | | | | | | | | | |
| 6. Actual weight of solids to be rotated/extracted (100 g min) | | | | | | | | | | |
| **Analyst's signature/date:** | | | | | | | | | | |

## Appendix B4.

| Client: | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample Number | | | | | | | | |
| A. Sample Description | | | | | | | | |
| 1. 100% Solids by observation | | | | | | | | |
| 2. ZHE NUMBER | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| 3. Weight of waste charged to ZHE (grams) | | | | | | | | |
| B. Extraction Fluid #3 addition | | | | | | | | |
| 1. Indicate volume of SPLP Extraction Fluid #3 (DI Water) added. (Usually 500 mL or 20 X A.3 if less than 25 g was used) | | | | | | | | |
| 2. Check for positve ZHE pressure | | | | | | | | |

| Client: | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sample Number | | | | | | | | |
| A. Sample Description (Continued from above) | | | | | | | | |
| 1. 100% Solids by observation | | | | | | | | |
| 2. ZHE NUMBER | 9 | 10 | 11 | 12 | | | | |
| 3. Weight of waste charged to ZHE (grams) | | | | | | | | |
| B. Extraction Fluid #3 addition (Continued from above) | | | | | | | | |
| 1. Indicate volume of SPLP Extraction Fluid #3 (DI Water) added. (Usually 500 mL or 20 X A.3 if less than 25 g was used) | | | | | | | | |
| 2. Check for positve ZHE pressure | | | | | | | | |

| C. Record of Extraction Period | Time: | Analyst's signature: | Date: |
|---|---|---|---|
| 1. Extraction Start Time | AM/PM | | |
| 2. Extraction Stop Time | AM/PM | | |
| 3. Min. ambient temperature | ° C | | |
| 4. Max. ambient temperature | ° C | | |

**Appendix B5.**

| TCLP/SPLP Extraction Device Rotation Speed | | |
|---|---|---|
| **Unit I.D.** | **Speed (RPM)** | **Initial and Date** |
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| *Acceptance criteria: 28 to 32 rpm.* | | |

# APPENDIX C.

## SAMPLE COLLECTION, PRESERVATION, AND HANDLING.

C.1 All samples will be collected using an appropriate sampling plan.

C.2 The SPLP may place requirements on the minimum size of the field sample, depending upon the physical state(s) of the sample and the analytes of interest. An aliquot will be needed for the preliminary evaluation of which extraction fluid is to be used (for the non-volatile extraction procedure). Another aliquot may be needed to actually conduct the non-volatile extraction. Another aliquot may be needed for the analysis of volatile organics. Quality control measures may require additional aliquots. Further, additional sample may be useful in case the initial testing is not acceptable.

C.3 Preservatives are not added to samples before extraction.

C.4 Samples may be refrigerated, unless refrigeration results in irreversible physical changes to the sample. If precipitation occurs, the entire sample (including precipitate) should be extracted.

C.5 Care must be taken to minimize the loss of volatile components when the sample is to be evaluated for volatile analytes. Samples should be collected and stored in a manner intended to prevent the loss of volatile analytes (*e.g.* samples should be collected in Teflon-lined septum capped vials and stored under refrigeration; samples should be opened only immediately prior to extraction).

C.6 SPLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH less than 2, unless precipitation occurs. Extracts should be preserved for other analytes according to the guidance given in the individual analytical methods. Extracts or portions of extracts for organic analyte determinations will not be allowed to come into contact with the atmosphere (*e.g.* no headspace) to prevent losses.

C.7 Samples must undergo SPLP extraction within the following time periods indicated below. If sample holding times are exceeded, the values obtained will be considered minimum concentrations. Exceeding the holding time is not acceptable in establishing that a sample does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the sample exceeds the regulatory level.

**MAXIMUM HOLDING TIME FOR SAMPLES**

| **Analytes** | From field collection | From SPLP extraction | From preparative extraction | **Total elapsed time** |
|---|---|---|---|---|
| | To SPLP extraction | To preparative extraction | To determinative analysis | |
| Volatiles | 14 | n/a | 14 | 28 |
| Semi-volatiles | 14 | 7 | 40 | 61 |
| Metals, except Hg | 180 | n/a | 180 | 360 |
| Mercury | 28 | n/a | 28 | 56 |

# APPENDIX D.

## METHOD OF STANDARD ADDITIONS.

D.1 The method of standard additions requires preparing calibration standards in the sample matrix rather than in reagent water or blank solution. Four (4) identical aliquots of a sample are prepared, 3 of which contain known amounts of standard added. The first addition should be prepared so that the concentration added is about 50% of the expected concentration of the (unspiked) sample. The second and third additions should be prepared so that the concentrations added are approximately 100% and 150% of the expected concentration. All 4 aliquots are maintained at the same final volume by addition of reagent water or a blank solution. The aliquots may need further dilution to maintain the concentrations in the linear range of the analytical method.

D.2 A graph is prepared plotting the analytical response against the concentration of standard added. Linear regression analysis on the data is performed, and the negative of the x-axis intercept is the concentration of the analyte in the unspiked sample.

D.3 Alternatively, subtract the instrumental signal, or external-calibration-derived concentration, of the unknown (unspiked) sample from the instrument signals (or external-calibration-derived concentrations) of the spiked samples. Plot the resultant instrument signals or concentrations versus the concentrations of standard added added and perform linear regression. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

Copy #: 9040-____

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## THE DETERMINATION OF pH

## GLA 9040 BG

Revision 2.0

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of aqueous and solid samples for pH. This SOP is an interpretation of SW-846 methods 9040B, 9041, and 9045C, and Standard Methods no. 4500-$H^+$. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

## 1.1 MATRICES

This method is applicable to aqueous wastes and multiphasic wastes where the aqueous phase constitutes at least 20% of the total volume of the sample. In addition, samples may be solids, sludges, or non-aqueous liquids, with water less than 20% of the total volume. Samples should be analyzed as soon as practical.

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

The pH values of samples are determined electrometrically using either a glass electrode in combination with a reference potential, or a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH. Aqueous samples are analyzed directly, solid samples are mixed with water and the pH of the aqueous portion determined. Alternatively, samples which might damage or seriously coat the electrode (ex., oils) are prepared appropriately and the pH is determined by a pH-sensitive paper.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

## 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

## 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

# 4.0 INTERFERENCES

4.1 Glass electrodes are generally not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants, or moderate (< 0.1 M) salinity.

4.2 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, or sonication, followed by rinsing with distilled water. An additional treatment with 10% hydrochloric acid may be necessary to remove any remaining film.

4.3 Samples with very low or very high pH may give incorrect readings on the meter. Strongly basic solutions, with a true pH >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strongly acidic solutions, with a true pH <1, may give incorrectly high pH measurements.

4.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference is controlled with instruments with temperature compensation or by calibrating the system at the temperature of the samples. The second source of temperature effects is the change in pH due to changes in the sample as the temperature changes. This error is sample dependent and cannot be controlled. It should be noted by reporting both the pH and temperature at the time of analysis.

4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in reagent and sample preparations. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with water. Periodic cleaning of sample preparation and analysis areas, including replacement of severely contaminated benchtop covers, will be performed.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed, as well as daily checks of the conductance meter and reagent water supplies.

5.2 pH Log Book:

A log book will be maintained for all pH determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Analyst's signature and date
- Sample temperatures
- Check standard identifier
- LIMS batch reference number
- Reviewer's signature and date

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out. Daily water supply monitoring results are recorded in a separate book.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

## 6.0 QUALITY CONTROL

### 6.1 Meter Calibration Verification

The pH meter is calibrated each day of use (see Section 11.1). After the calibration is performed, it is verified upon each use during the course of the day. A 7.0 calibration buffer solution is read, and must be 95 to 105% of 7.0. If this is not obtained, the metere is recalibrated using fresh buffer solutions.

### 6.2 Check Standard

A 7.0 calibration buffer solution is read before any sample pH readings are taken, and the reading must be 7.0 ±0.1 pH units. This check standard is analyzed at the beginning and end of each set of 20 or less samples. If the check standard does not meet the acceptance criteria, the meter is recalibrated and the effected samples are reanalyzed.

### 6.3 Duplicate Samples

With each set of 20 or less samples per matrix, a sample is analyzed in duplicate. A ±10% relative percent difference (RPD) is used as a guideline for replicate readings. If the duplicate analysis does not meet this criteria, corrective action must occur, which may include reanalysis of the samples or qualifying the effected sample results.

### 6.4 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

### 6.5 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result out of control.
- A deviation from the normal SOP for the method is discovered, and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

## 7.0 SAMPLE MANAGEMENT

**7.1** The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

**7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "WETC". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in a QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Corrective action sheets.

### 8.2 Quality Assurance Program

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Plan.)

## 9.0 EQUIPMENT

9.1 *pH meter and probe - glass electrode with reference, or combination probe, Fisher Accumet 25, or equivalent.*
9.2 Magnetic stirrer and Teflon-coated stir bars.
9.3 Beakers, 250-mL size.
9.4 Thermometer, minimum calibrated range of 10-30°C.
9.5 Analytical balance, capable of weighing to the nearest 0.1 g.

## 10.0 STANDARDS AND REAGENTS

10.1 ASTM Type II reagent water (DI water).
10.2 Standard buffer solutions - commercially available solutions that have been validated by comparison to NIST standards; examples, Fisher no. SB101 (pH 4), no. SB107 (pH 7), and no. SB115 pH 10).

## 11.0 PROCEDURE

### 11.1 CALIBRATION

The instrument/electrode system is calibrated with a minimum of two buffer solutions that bracket the expected pH values of the samples, and are approximately 3 pH units apart. The pHs of the calibration buffer solutions are 4.0, 7.0, and 10.0. Adjustments are made until readings of the buffer solutions are within 0.05 pH units of expected values. This calibration is performed daily when samples are analyzed.

**NOTE:** If an accurate pH reading based on the conventional pH scale of 0 to 14 at 25°C is required, the analyst should control sample temperature at 25±1°C when sample pH approaches the alkaline end of the scale (pH ≥ 11).

### 11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.2.1 Liquids - Aliquot 50 to 100 mL of sample into a clean 250-mL beaker, and add a clean magnetic stir bar. Prepare one sample, per twenty or less, in duplicate.

11.2.2 Soils/Solids - Weigh 20 to 50 g of sample into a clean 250-mL disposable beaker, and add an equal amount of reagent water and a clean magnetic stir bar. Mix thoroughly for five minutes, and allow to settle for about 60 minutes. Prepare one sample, per twenty or less, in duplicate.

11.2.3 Non-aqueous liquids/Wastes – Aliquot 20 to 50 g of sample into a clean 250ml disposable beaker and add an equal amount of reagent water and a clean magnetic stir bar. Mix thoroughly for five minutes, and allow to settle for about 15 minutes. Prepare one sample, per twenty or less, in duplicate.

### 11.3 ANALYSIS OF SAMPLES

11.3.1 After the meter has been calibrated, rinse the electrodes thoroughly with reagent water and place into the pH 7.0 buffer solution. Allow reading to stabilize, and record pH and temperature. Rinse the electrode with reagent water.

11.3.2 For aqueous liquids, immerse the electrode into the sample and gently stir. After the reading has stabilized, record the pH and the temperature. Rinse the electrode thoroughly between each sample reading.

11.3.3 For soils/solids, immerse the electrode just below the suspension without stirring, and record the pH and temperature. Rinse the electrode thoroughly between each sample reading.

11.3.4 For non-aqueous/waste samples, immerse the electrode into the water layer without stirring, and record the pH and temperature. Rinse the electrode thoroughly between each sample reading. For samples that have potential of damaging the electrode, the pH is read using pH paper.

11.3.3 Analyze the pH 7.0 buffer between each batch of 20 samples, and record pH and temperature. Also, analyze the pH 7.0 buffer and the sample duplicates at the end of any batch of samples.

11.3.4 For solids, report the result as "waste pH measured in water at 25°C".

**NOTE:** If the sample temperature differs by more than 2°C from the buffer solutions, the pH values must be corrected by automatic or manual temperature compensation.

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 13.0 REFERENCES

13.1 SW-846 Methods 9040B: pH Electrometric Measurement.
13.1 SW-846 Methods 9045C: Soil and Waste pH.
13.2 Method 4500-$H^+$: pH Value, Sections A (Introduction) and B (Electrometric Method); Standard Methods for the Examination of Water and Wastewater, 18$^{th}$ Edition, 1992.
13.3 Great Lakes Analytical Quality Assurance Program Manual.
13.4 Great Lakes Analytical Chemical Hygiene Plan.
13.5 Great Lakes Analytical SOP for Login Department.
13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

Copy #: 160.1/4-_____

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## THE DETERMINATION OF TOTAL SOLIDS, TOTAL DISSOLVED SOLIDS, TOTAL SUSPENDED SOLIDS, TOTAL VOLATILE SOLIDS/PERCENT ASH, FRACTIONAL ORGANIC CARBON, and ASTM TOTAL ORGANIC CARBON

## GLA 160.1/4 BG

Revision 2.0

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/25/99

Laboratory Director: _____ Date: 5/28/99

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of samples for total solids (residue), total dissolved (filterable) solids, total suspended solids, and/or total volatile solids. This SOP is an interpretation of the EPA Methods 160.1, 160.2, 160.3, and 160.4, Standard Methods no. 2540, sections B, C, D, and E, ASTM D2974-87, and Method SW-846 5035 Section 7.5. Instructions for the determination of free liquids in waste samples by the paint filter test are also included (Method SW846 9095A).

## 1.1 MATRICES

This procedure is applicable for the analysis of soils, solid waste, drinking, surface, and saline waters,and domestic and industrial wastes.

***NOTE:*** *Preservation of the sample is not practical or required, although analysis should begin as soon as possible.* Refrigeration at 4°C to minimize microbiological decomposition of solids is recommended.

## 1.2 REGULATORY APPLICABILITY

40 CFR 121

# 2.0 SUMMARY

**2.1** Filterable (dissolved solids) residue (EPA 160.1, SM 2530-C): Filterable residue are those solids capable of passing through a glass fiber filter and being dried to constant weight at 180°C. A well-mixed aliquot of sample is filtered through a glass fiber filter. The filtrate is evaporated and the solids dried to constant weight at 180°C. The practical range of this determination is 10 to 20,000 mg/L. The solids retained on the filter may be dried at 103-105°C, and weighed for the determination of total suspended solids.

**2.2** Non-filterable (suspended solids) residue (EPA 160.2, SM 2530-D): Non-filterable residue are those solids which are retained by a glass fiber filter and dried to constant weight at 103-105°C. A well-mixed sample is passed through a glass fiber filter, and the residue retained on the filter dried to constant weight at 103-105°C. The practical range of this determination is 4 to 20,000 mg/L.

**2.3** Total residue (Total Solids or % Dry Weight; EPA 160.3, SM 2530-B, SW846 5035 Sec. 7.5): Total residue is the sum of the homogeneous suspended and dissolved materials in a sample. A well-mixed aliquot of sample is quantitatively transferred to a pre-weighed evaporating dish and evaporated to dryness at 103-105°C. The practical range of this determination is 10 to 20,000 mg/L.

**NOTE:** The results of the total filterable (dissolved) and total non-filterable (suspended) solids analyses CANNOT be mathematically added to obtain a total solids result.

**2.4** Volatile residue (EPA 160.4, SM 2530-E): The dried residue obtained from the determination of total, filterable, or non-filterable residue is ignited at 550 $\pm$ 50°C in a muffle furnace for one hour or until all organic matter has ashed off. The remaining solids represent the fixed solids, while the weight lost on ignition is the volatile solids.

**2.5** ASTM Fractional/Total Organic Carbon (ASTM D2974-87): Samples are prepared the same as for volatile residue, and ignited at 440 $\pm$ 50°C for a minimum of one hour or until all organic matter has ashed off and the sample is at a constant weight.

2.6 Paint filter liquids test (SW846 9095): A 100g sample is placed in a paint filter. If any liquid passes through and drops from the filter with 5 minutes, the material is considered to contain free liquids.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents.

## 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

## 3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

## 3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

## 3.5 HIGH TEMPERATURES AND MUFFLE FURNACE

3.5.1 High temperature gloves and tongs must be used when loading/unloading samples from the muffle furnace. Special care should be exercised in handling any sample which has not completely evaporated or combusted to prevent splashing of hot materials.

3.5.2 The muffle furnace is operated at a temperature of 400 - 600°C for the duration of this test. Contact with the heated surfaces of the furnace or sample crucibles can cause second and third degree burns as well as melt inappropriate materials onto the analyst's hands or arms if allowed to get too close. Appropriate high temperature gloves and long tongs are provided for loading and unloading the muffle furnace.

3.5.3 When analyzing anything but soils for total volatile solids, the muffle furnace must be relocated to in front of a fume hood. Fumes given off by the evaporation/combustion of samples during the ignition process can then be appropriately vented outside the lab.

3.5.4 Incomplete combustion of especially high organic bearing samples can saturate the air inside of the muffle furnace. If the door is opened under these conditions, a flash fire could occur due to the rapid oxidation of the organic laden atmosphere. The analyst must allow the samples the minimum one hour of ignition time after loading the furnace to insure all organics have been combusted before opening the muffle furnace door.

## 4.0 INTERFERENCES

4.1 The principle source of error in these determinations is failure to obtain a representative sample. The analyst must be sure a representative portions of well-mixed samples are taken for analysis.

4.2 Highly mineralized waters and sludges containing significant amounts of calcium, magnesium, chloride or sulfate may be hygroscopic and will require prolonged drying, dessication, and rapid weighing. Non-representative solids, such as leaves, sticks, fish, etc., should be excluded from the sample if their inclusion is not representative of the material being sampled or desired in the final result. Too much residue in the drying dish may crust over and entrap water (total residue should be limited to about 200 mg).

4.3 Filterable (dissolved) solids - Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to ensure that all bicarbonate is converted to carbonate.

4.4 Non-filterable (suspended) solids - Samples high in filterable solids, such as saline waters, brines, and some industrial wastes, may exhibit a positive interference. Thoroughly wash the filter to ensure removal of dissolved materials.

4.5 Total solids/% Dry Weight - Floating oil and grease should be dispensed with a blender before analysis. Results from samples still containing non-volatile liquids, such as oils, after the appropriate drying time must be flagged: *"total solids partially due to liquids non-volatile at 103-105°C".*

4.6 Total volatile solids - This test is subject to errors including: loss of water of crystallization, loss of organic matter prior to combustion, incomplete oxidation of organics, and decomposition of mineral salts. Therefore, the results cannot be considered an accurate measure of organic carbon in the sample.

4.7 Paint filter test - This test must be performed above the freezing point of any liquid in the sample.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 Solids Log Book(s):

A log book will be maintained for all determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume **and** weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Data reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and LCS duplicate info
- Final weights
- Initial and final furnace temps

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

# 6.0 QUALITY CONTROL

## 6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a 5 % frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), and LCS duplicates. The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

## 6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

## 6.3 LABORATORY CONTROL SAMPLES (LCS) AND LCS DUPLICATES

An external reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e. minimum 5 % frequency*). The results of the samples must have recoveries within established control limits, or where there is not enough data to calculate control limits, within 20 % of the known value. The relative percent difference (%RPD) between the LCS and LCS duplicates must be within established control limits, or where there is not enough data to calculate control limits, within 20 % RPD.

## 6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

## 6.7 CORRECTIVE ACTION

A Corrective Action Report must be initiated any time the quality of the data could be questioned, or more specifically, when any of the following occur:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

# 7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "xxxx" and "xxxx"?. The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Control Manual.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.
- Corrective action sheets.

### 8.2 INTERNAL AUDITS AND PERFORMANCE EVALUATION SAMPLES

Internal audits will be performed periodically to assess analytical system performance. These audits will be followed up to ensure that any deficiencies found have been eliminated and/or rectified. Performance evaluation samples will be periodically to assess laboratory performance (Refer to xxx)

## 9.0 EQUIPMENT

9.1 Glass evaporating dishes or porcelain crucibles, approx. 130 mL capacity.
9.2 Aluminum weighing dishes, numbered and categorized.
9.3 Porcelain Gooch crucibles.
9.4 Glass fiber filter disks, without binder, Gelman A/E or equivalent.
9.5 Suction flask, adapter and vacuum pump.
9.6 Drying oven, 103-105°C/180°C, with monitoring thermometer.
9.7 Analytical balance capable of weighing to 0.0001 g (0.1 mg).
9.8 Graduated cylinders, 25-250 mL size.
9.9 Dessicator.
9.10 Muffle furnace capable of attaining 550 ± 50°C.
9.11 Polypropylene sample cups.

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II water (DI water).
10.2 Sodium Chloride - NaCl, crystal, Fisher no. xxx, or Mallinckrodt no. xxx.
10.3 Clean dry sand, purchased, Fisher no. xxx, or Mallinckrodt xxx.
10.4 Sodium chloride standard solution, 2000 mg/L NaCl - Accurately weigh approximately 2.0 g of NaCl and transfer to a 1000-mL volumetric flask. Dissolve, dilute to the mark with reagent water, and mix. Transfer to a 1-L plastic bottle. Keep tightly capped to minimize evaporation and subsequent concentration of the standard. Prepare solution annually or as needed.

## 11.0 PROCEDURES

**NOTE:** Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

### 11.2 PREPARATION OF EVAPORATING DISHES

11.2.1 For analysis of filterable and/or non-filterable solids, see section 11.3.

11.2.2 For analysis of total solids/% Dry Weight:

- Aluminum weighing dishes for solids are cleaned and rinsed with reagent water, dried in the oven at 103-105°C for a minimum of 1 hour, cooled and dessicated for a minimum of two hours before use.
- Glass evaporating dishes used for waters are cleaned and rinsed with reagent water, dried in the muffle furnace at 350°C for a minimum of 1 hour, cooled and dessicated for a minimum of two hours before use.
- Porcelain crucibles are used for non-aqueous liquids and non-aqueous liquid containing waters and sludges. They are cleaned and rinsed with reagent water, dried in the oven at 103-105°C for a minimum of 1 hour, cooled and dessicated for a minimum of two hours before use.

11.2.3 For analysis of total volatile solids (only): Porcelain crucibles are used for analysis of total volatile solids. They are cleaned and rinsed with reagent water, then ignited in a muffle furnace at 550 ± 50°C for 1 hour, cooled and dessicated for a minimum of two hours before use.

11.2.4 For analysis of total volatile solids following analysis for dissolved or suspended solids: All porcelain Gooch and evaporating crucibles must be thoroughly cleaned with detergent and water, final rinsed with reagent water, then ignited in a muffle furnace at 550 ± 50°C for 1 hour, cooled and dessicated for a minimum of two hours before use.

11.2.5 Weigh each evaporating dish, crucible, or filter assembly, required for all QC and test samples, to the nearest 0.0001 g and record the crucible I.D.'s and weights in the appropriate log book.

### 11.3 PREPARATION OF FILTRATION ASSEMBLY

11.3.1 Gooch crucibles must be thoroghly cleaned before each use. If grease or oily coatings are not removed by normal cleaning with detergent and reagent water, or if the samples are also to be analyzed for total volatile solids, they should be ignited in a muffle furnace at 550 ± 50°C for 1 hour and cooled before use.

11.3.2 Place a glass fiber filter disk, wrinkled side up, in the Gooch crucible. Wet the disk with about 5ml of reagent water to seat in the bottom of the crucible. Place crucible into the adapter and apply vacuum. Wash with three (3) successive volumes of reagent water and continue to apply vacuum until all traces of water have passed through.

11.3.3 If samples are to be analyzed for total filterable (dissolved) solids only, proceed to section 11.3.4. Else, dry crucible and filter together in the oven at 103-105°C for a minimum of two hours. Remove to dessicator for one hour and weigh to the nearest 0.0001 g. Repeat cycle until a constant weight is obtained. Alternatively, prepare crucibles and filter and allow to dry in the oven at 103-105°C overnight. Remove, and place in the dessicator for at least 1 hour before use.

11.3.4 Weigh each evaporating dish, crucible, or filter assembly, required for all QC and test samples, to the nearest 0.0001 g and record the crucible I.D.'s and weights in the appropriate log book.

## 11.4 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.4.1 For Method Blanks:

- Liquid samples
  - * For filterable (dissolved) and non-filterable (suspended) solids, 100 mL of reagent water is processed as a sample.
  - * For total solids and volatile solids, aliquot 50 mL of reagent water into a prepared, pre-weighed glass evaporating dish (if for analysis of volatile solids only, use a porcelain crucible). Record the weight of water and dish to the nearest 0.0001 g.
- Solid samples
  - * For total solids and volatile solids, aliquot 10 mL of reagent water into a prepared, pre-weighed aluminum evaporating dish (if for analysis of volatile solids only, use a porcelain crucible). Record the weight of water and dish to the nearest 0.0001 g.
  - * Filterable and non-filterable solids are not determined for solid samples.

11.4.2 For Laboratory Control Samples (samples contain xx xx xx).

- Liquid samples
  - * For analysis of filterable solids (only), process two 100-mL aliquots of sodium chloride solution as samples.
  - * For non-filterable solids (only), weigh approximately 0.1 g of clean sand into a weigh boat. Record the actual weight. Quantitatively rinse the sand into a clean sample cup with approximately 100 mL of reagent water. Prepare two of these spikes for analysis and process as samples.
  - * For filterable and non-filterable solids, weigh approximately 0.1 g of clean sand into a weigh boat. Record the actual weight. Quantitatively rinse the sand into a clean sample cup with a 100-mL aliquot of sodium chloride solution. Prepare two of these spikes for analysis and process as samples.
  - * For total and volatile solids, aliquot 50 mL of sodium chloride solution into a prepared, pre-weighed glass evaporating dish (if for analysis of volatile solids only, place solution in a porcelain crucible). Record the volume of solution, and the weight of the solution and dish to the nearest 0.0001 g.
- Solid samples
  - * For total and volatile solids, weigh approximately 10 g of sand into a prepared, pre-weighed aluminum evaporating dish (if for analysis of volatile solids only, place sand in a porcelain crucible). Record the volume of solution, and the weight of the sand and dish to the nearest 0.0001 g. Add approximately 5 mL of reagent water.
  - * Filterable and non-filterable solids are not determined for solid samples.

11.4.3 *For Test Samples:*

There are no specific preparations of the samples other than thorough mixing immediately prior of analysis. Analyst observation is usually adequate for determining the proper amount of sample to use.

- Liquid samples
  - * For analysis of filterable (dissolved) and non-filterable (suspended) solids:
    - Filtration time should not exceed 10 minutes for samples containing high levels of suspended samples.
    - A larger sample must be used (250-500 mL) for samples with minimal amounts of suspended solids. The captured weight of solids must be at least 1.0 mg, or the data must be flagged as "insufficient sample to meet minimum method criteria."
  - * For total and volatile solids, place approximately 50 mL of sample into a prepared, pre-weighed glass evaporating dish (if for analysis of volatile solids only, place solution in a

porcelain crucible). Record the volume of solution, and the weight of the solution and dish to the nearest 0.0001 g. For other aqueous liquids, aliquot 100 mL of samples with minimal amounts of solids apparent - use smaller volumes if solids are visible,

- Solid samples
  * For total and volatile solids, place approximately 10 g of sample (including non-aqueous liquid samples) into a prepared, pre-weighed aluminum evaporating dish (if for analysis of volatile solids only, place sand in a pre-weighed porcelain crucible). Record the volume of solution, and the weight of the sand and dish to the nearest 0.0001 g.
  * Filterable and non-filterable solids are not determined for solid samples.

11.4.4 Matrix spiked samples are not applicable nor required for these methods.

## 11.5 FILTRATION PROCEDURE FOR DISSOLVED AND SUSPENDED SOLIDS

11.5.1 Each sample/blank/spike is processed in turn by this procedure. Please note that some sections are not required depending upon the analyses being performed.

11.5.2 Inspect the crucible/filter assembly and insure that the filter is centered in the bottom of the crucible. Wet the filter with a small amount of reagent water to effect a good seal upon the application of vacuum.

11.5.3 ***For samples to be analyzed for total dissolved solids***: Thoroughly clean the filtration flask, funnel and adapter with a final reagent water rinse before ***EVERY*** sample filtration.

9.8.2.2 Fit the crucible into the adapter of the filtration apparatus and switch on the vacuum pump.

11.5.3 Shake the sample container vigorously and ***IMMEDIATELY*** transfer a predetermined aliquot volume into the crucible using an appropriately sized, clean graduated cylinder. Remove all traces of water by allowing suction to remain on after the sample has passed through.

11.5.4 Rinse the sample with three successive washings of reagent water, approximately 10 mL per rinse. Be sure to rinse any droplets or particulates adhering to the sides of the crucible down into the filter as well, allowing for complete drainage between washings. Remove all traces of water by continuing to apply vacuum after water has passed through.

11.5.5 Switch off pump and allow vacuum to slowly release. Carefully remove the crucible from the adapter.

11.5.6 ***For samples to be analyzed for total dissolved solids***: Quantitatively transfer the filtrates to appropriate evaporating dishes.

11.5.7 Proceed to section 11.6 for filterable solids, or 11.7 for non-filterable solids.

## 11.6 ANALYSIS FOR TOTAL FILTERABLE (DISSOLVED) SOLIDS

11.6.1 After transferring all samples to their respective evaporating dishes, dry the evaporating dishes in the oven at 103-105°C until all water is evaporated. This will probably take overnight.

11.6.2 Raise the oven temperature control to 180°C. When the temperature reaches and stabilizes at 180°C, record the initial oven temperature.

11.6.3 Dry the evaporating dishes in the oven at 180°C for a minimum of 1 hour. Samples exhibiting substantial amounts of dissolved solids should be allowed to dry for a longer period of time (even overnight) to evaporate potentially entrapped water and convert any bicarbonate to carbonate.

11.6.4 Record the final oven temperature. Remove dishes to the dessicator for at least 1 hour before weighing. Record final weight to the nearest 0.0001 g.

## 11.7 ANALYSIS FOR TOTAL NON-FILTERABLE (SUSPENDED) SOLIDS

11.7.1 Record the initial oven temperature.

11.7.2 Dry the gooch crucibles in the oven at 103-105°C for a minimum of 1 hour. Alternatively, allow the samples to dry in the oven at 103-105°C overnight.

11.7.3 Record the final oven temperature.

11.7.4 Remove the crucibles to dessicator for at least 1 hour, and weigh to the nearest 0.0001 g. If samples were dried overnight, record this as the final weight. If samples have been in the oven for the minimum 1 hour time period, repeat the drying/cooling/weighing cycle until a constant weight is obtained. Record this final weight.

## 11.8 ANALYSIS FOR TOTAL SOLIDS

11.8.1 Record initial temperature of oven.

11.8.2 Place all evaporating dishes in the oven at 103-105°C for a minimum of 4 hours for solid samples, or overnight (minimum of 8 hours) for waters and/or solids.

11.8.3 Record final temperature of oven.

11.8.4 After checking any waters for complete evaporation, remove samples from the oven and dessicate for at least one hour.

11.8.5 Weigh each sample/dish and record the final weight to the nearest 0.0001 g.

11.8.6 Analysis for **total solids** is complete at this step. Continue with section 11.9 for the analysis of **total volatile solids (TVS), % Ash, Organic Carbon Content (OCC), Fractional Organic Carbon (FOC), and ASTM Total Organic Carbon (TOC)**, if required.

## 11.9 ANALYSIS FOR TOTAL VOLATILE SOLIDS

**NOTE:** If any sample is suspected of having a high organic content that might produce large volumes of smoke or other fumes upon combustion, remove the muffle furnace to a laboratory cart and place in front of a fume hood in the inorganic lab area.

11.9.1 Adjust the muffle furnace temperature to 550 $\pm$ 50°C for TVS/%Ash, and to 440 $\pm$ 50°C for FOC,OCC, and ASTM TOC. Record the initial temperature of the muffle furnace.

11.9.2 *While wearing high temperature gloves and using long tongs,* load the QC and test samples into the muffle furnace. Due to space limitations in the muffle furnace, large numbers of samples will require that several "batches" be ignited separately. Be sure the muffle furnace door is closed completely and the latch is engaged.

11.9.3 Heat samples for one hour. **CAUTION: Do not open the muffle furnace door during this time**. The potentially vapor saturated could create a flash fire upon the inrush of air (oxygen).

11.9.4 After one hour, open the muffle furnace and observe the samples. If all the organic material has ashed off, go to section 11.9.5. If not, continue ignition for an additional one hour.

11.9.5 After one hour, record the final temperature of the muffle furnace.

11.9.6 Remove samples from the furnace and dessicate for at least one hour.

11.9.7 Weigh each sample/dish and record the final weight to the nearest 0.0001 g.

## 11.10 CALCULATIONS

11.10.1 Total filterable (dissolved) solids:

$$\textit{Filterable solids, mg/L} = \frac{[\textit{initial wt. (g)} - \textit{final wt. (g)}] \times 1{,}000{,}000}{\textit{volume of sample used (mL)}}$$

11.10.2 Total non-filterable (suspended) solids:

$$\textit{Non-filterable solids, mg/L} = \frac{[\textit{initial wt. (g)} - \textit{final wt. (g)}] \times 1{,}000{,}000}{\textit{volume sample used (mL)}}$$

11.10.3 Total solids as percent solids - % for solids/non-aqueous liquids:

$$\textit{Percent total solids, \%} = \frac{[(C - A)] \times 100}{[(B - A)]}$$

where: A = initial tare weight of evaporating dish (g)
B = weight of dish AND sample before drying (g)
C = final weight of sample and dish after drying (g)

11.10.4 Total solids, as mg/kg, for solids - for solids/non-aqueous liquids:

$$\textit{Total solids, mg/kg} = \frac{[(C - A)] \times 1{,}000{,}000}{[(B - A)]}$$

where: A = initial tare weight of evaporating dish (g)
B = weight of dish AND sample before drying (g)
C = final weight of sample and dish after drying (g)

11.10.5 Total solids, as mg/L, for waters:

$$\textit{Total solids, mg/L} = \frac{[(C - A)] \times 1{,}000{,}000}{[(B)]}$$

where: A = initial tare weight of evaporating dish (g)
B = volume of sample used (mL)
C = final weight of sample and dish after drying (g)

11.10.6 Total volatile solids - % for solids or any liquids:

$$\textit{Percent volatile solids, \%} = \frac{[(C - D)] \times 100}{[(C - A)]}$$

where: A = initial tare weight of crucible (g)
C = final weight of sample and crucible after drying (g)
D = final weight of sample and crucible after ignition (g)

11.10.7 Percent ash, FOC,OCC, ASTM TOC (fixed solids) - % for solids or any liquids:

$$\textit{Percent ash, Percent Organic Carbon, \%} = \frac{[(D-A)] \times 100}{[(C-A)]}$$

where: A = initial tare weight of crucible (g)
C = final weight of sample and crucible after drying (g)
D = final weight of sample and crucible after ignition (g)

11.10.8 Total volatile solids (mg/L) for waters:

$$\textit{Total volatile solids, mg/L} = \frac{[(C-D)] \times 1{,}000{,}000}{[(B)]}$$

where: B = volume of sample used (mL)
C = final weight of sample and crucible after drying (g)
D = final weight of sample and crucible after ignition (g)

11.10.9 Total fixed solids (mg/L) for waters:

$$\textit{Total volatile solids, mg/L} = \frac{[(D-A)] \times 1{,}000{,}000}{[(B)]}$$

where: A = initial tare weight of evaporating dish (g)
B = volume of sample used (mL)
D = final weight of sample and crucible after ignition (g)

11.10.10 Calculation notes:

Any sample with liquid(s) (*e.g.* - oils or grease) which are not volatile at 103-105°C must be flagged "*total solids partially due to liquids non-volatile at 103-105°C*".

11.10.11 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.10.12 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

## 11.11 PAINT FILTER TEST

11.11.1 Assemble test apparatus as shown in Figure 1.

11.11.2 Place sample in filter. Settling the sample into the filter may be facilitated by lightly tapping the side of the filter/funnel.

**NOTE:** In order to assure uniformity and standardization of the test, materials which do not conform to the shape of the filter (such as sorbent pads or pillows) should be cut into small pieces using scissors, shears, or a knife. The integrity of the sorbent fabric should be preserved as much as possible. The particles to be tested should be reduced to about 9 mm in size. Grinding sorbent materials should be avoided as this may destroy the integrity of the sorbent and produce may "fine particles" which would not be normally present. Light crushing is acceptable for brittle materials larger than 1 cm that do not conform to the filter (such as clay, silica gel, and some polymers, which are not practical to cut).

11.11.3 Allow sample to drain for 5 minutes into the graduated cylinder.

11.11.4 If any portion of the test material collects in the graduated cylinder during the 5-minute period, the material is deemed to contain free liquids.

11.11.5 Any sample containing free liquids is reported as a "Fail". Samples that do not contain free liquids are reported as "Pass".

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 13.0 REFERENCES

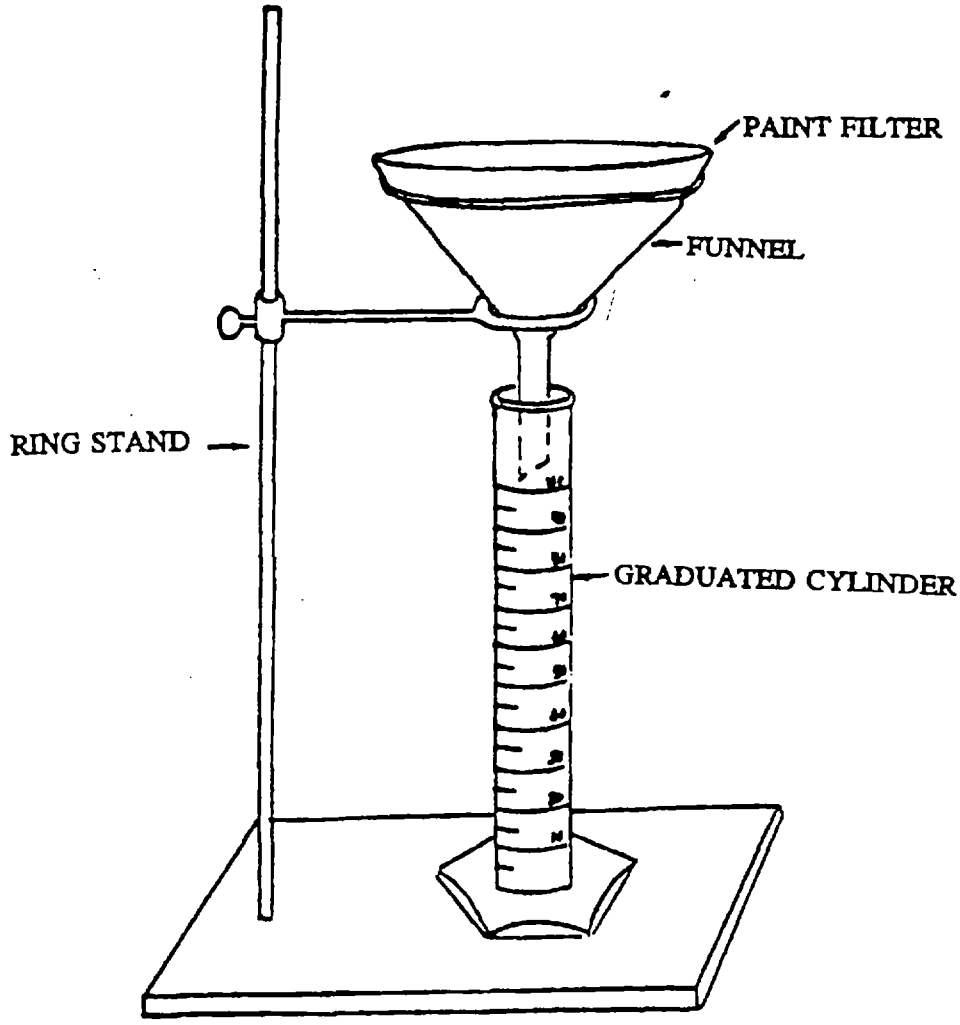
13.1 EPA Method 160.1: Residue, Filterable (Gravimetric, dried at 180°C).
13.2 EPA Method 160.2: Residue, Non-filterable (Gravimetric, dried at 103-105°C).
13.3 EPA Method 160.3: Residue, Total (Gravimetric, dried at 103-105°C).
13.4 EPA Method 160.4: Residue, Volatile (Gravimetric, ignition at 550°C).
13.5 Standard Methods no. 2540: Solids - section B, Total Solids Dried at 103-105°C.
13.6 Standard Methods no. 2540: Solids - section C, Total Dissolved Solids Dried at 180°C.
13.7 Standard Methods no. 2540: Solids - section D, Total Suspended Solids Dried at 103-105°C.
13.8 Standard Methods no. 2540: Solids - section E, Fixed and Volatile Solids Ignited at 500°C.
13.9 SW-846 Method 5035, Section 7.5, Dry Weight.
13.10 SW-846 Method 9095, Paint Filter
13.11 ASTM Method D2974-87, Total Organic Carbon
13.12 Great Lakes Analytical Quality Assurance Program Manual.
13.13 Great Lakes Analytical Chemical Hygiene Plan.
13.14 Great Lakes Analytical SOP for Login Department.
13.15 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

Refer to the Great Lakes Analytical Quality Assurance Program Manual.

**Figure 1.**

**Paint Filter Test Apparatus.**



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# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## THE DETERMINATION OF MERCURY IN

## LIQUIDS AND SOLIDS

## GLA 245.1/5 BG

Revision 2.1

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the determination of mercury by cold-vapor atomic absorption spectrophotometry. This SOP is an interpretation of EPA Methods 245.1 and 245.5, Standard Methods no. 3112, Section B, and methods SW-846 no's. 7470A and 7471A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

## 1.1 MATRICES

This SOP may be used for aqueous, solid, and mixed samples, including soils, sediments, sludge, domestic and industrial wastes. Concentration range for samples is typically 0.2 to 2.5 ppb. Higher concentrations may be determined by sample dilution.

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

Liquid samples are digested with nitric and sulfuric acids, potassium permanganate and potassium persulfate. Solid samples are digested with *aqua regia* (nitric and hydrochloric acids) and potassium permanganate. A series of standards is digested and analyzed concurrently to produce a calibration curve from which sample results are determined.

A semi-automatic cold-vapor apparatus is used to produce metallic mercury vapor from the resultant digestates: The sample is automatically mixed with hydrochloric acid and stannous chloride solution. The mercury is reduced to the elemental state which is then bubbled out of solution and carried into the instrumental light path by means of an inert argon gas flow. The atomic absorption of this vapor is read at 253.7 nm. Deuterium arc background correction is used to automatically correct for interference due to water vapor, chlorine, or other contaminants which absorb or block light at this wavelength. The absorption read by the spectrophotometer is proportional to the concentration of mercury in the original sample.

See Appendix A for method exceptions.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical (GLA) Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling chemicals and reagents.

## 3.2 CHEMICAL HYGIENE PLAN

The GLA Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

### 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

### 3.4 METHOD SPECIFIC CHEMICALS

Potassium permanganate and persulfate are strong oxidizers. They can burn eyes and skin. Also, they can cause a fire if mixed with incompatible chemicals.

## 4.0 INTERFERENCES

4.1 Potassium permanganate is added to eliminate any possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere.

4.2 Concentrations of copper as high as 10 mg/L do not interfere. Higher concentrations may cause interference.

4.3 Samples containing high levels of chlorides (such as sea water, brine, and industrial effluents) may require additional permanganate. Chlorides are converted to free chlorine, which also absorbs at 253 nm. Chlorine is eliminated before the reduction of mercury by using an excess of hydroxylamine reagent.

4.4 Certain volatile organic materials that absorb in the 253 nm region may also cause interference. A preliminary run without reagents should determine if this type of interference is present in samples. Deuterium arc background correction is used to automatically correct for these interferences.

4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water. Periodic cleaning of sample preparation and analysis areas will be performed.

## 5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 Mercury Log Book:

A log book will be maintained for all mercury determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- GLA Sample I.D. (one complete for each set)
- Initial sample volume or weight used
- Final volume of digestates
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Reviewer's signature and date
- Time/temperature of water bath (initial and every 30 minutes)
- Calibration standard identifiers and concentrations
- All readings, dilution factors, and calculated results

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

# 6.0 QUALITY CONTROL

## 6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5 % frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

## 6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

## 6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5 % frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15 % of the known value.

## 6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5 % (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25 % of the known value.

## 6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

## 6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

### 6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

## 7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for mercury analysis are queued under "xxxx"=FLAA. The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

## 8.0 METHOD VALIDATION

### 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

### 8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

### 8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the 7 replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for 7 replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

## 9.0 EQUIPMENT

9.1 Atomic absorption spectrophotometer - fitted with a mercury hollow cathode lamp, capable of allowing the absorption cell to be mounted in a stable fashion in the light path of the instrument, Varian 600 DBQ, and able to correct for non-atomic absorption at the selected analytical wavelength, or equivalent.
9.2 Absorption cell - 10 cm long with UV-transparent quartz windows.
9.3 Cold mercury vapor generator - for proper proportional mixing of mercury reducing agents and physical vapor generation, Varian VGA 77, or equivalent.
9.4 300-mL capacity BOD bottle with stoppers.
9.5 Hot plate/water bath - capable of maintaining 95°C
9.6 Thermometer - to accurately monitor the water bath for range 95-100°C.
9.7 Graduated cylinders, 100-mL size.
9.8 Pipettors and tips, 5-10 mL size.
9.9 Analytical balance capable of weighing to nearest 0.1 g.
9.10 5-20 mL dispensers with bottle.

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II or equivalent (DI water).
10.2 Sulfuric acid - concentrated $H_2SO_4$, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.3 Nitric acid - concentrated $HNO_3$, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.4 Hydrochloric acid - concentrated HCl, Fisher no. A508. **CAUTION:** Hydrochloride acid is corrosive.
10.5 Aqua regia, 50% - Prepare immediately before use. First, make aqua regia by carefully adding 3 volumes of concentrated HCl to 1 volume of concentrated $HNO_3$. Then mix equal volumes of the aqua regia with reagent water. **CAUTION:** Aqua regia gives off extremely corrosive, irritating fumes. All handling of aqua regia should be performed in a fume hood.
10.5 Hydrochloric acid, 5 N - Dilute 40 mL of concentrated HCl to 100 mL with reagent water.
10.6 Hydrochloric acid, 20% v/v - Dilute 20 mL of concentrated HCl to 100 mL with reagent water.
10.7 Potassium permanganate - $KMnO_4$ crystals, Fisher no. P279, or Mallinckrodt no. 7068. **CAUTION:** Oxidizer.
10.8 Potassium permanganate solution - Dissolve 5 g of $KMnO_4$ per 100 mL of reagent water.
10.9 Potassium persulfate - $K_2S_2O_5$, crystal, Merck no. PX1560-1, or Mallinckrodt no. 7076. **CAUTION:** Oxidizer.
10.10 Potassium persulfate solution - Dissolve 5 g of $K_2S_2O_5$ per 100 mL of reagent water.
10.11 Hydroxylamine hydrochloride - $NH_2OH{\cdot}HCl$, crystals, Fisher no. H330, or Mallinckrodt no.
10.12 Sodium chloride - NaCl crystals, Fisher no. S271, or Mallinckrodt no. 7581.
10.13 Hydroxylamine hydrochloride solution - Dissolve 12 g of $NH_2OH{\cdot}HCl$ and 12 g of NaCl per 100 mL of reagent water.
10.14 Stannous chloride, dihydrate - Tin (II) chloride dihydrate, $SnCl_2 \cdot 2\ H_2O$, crystals, Fisher no. T142, or Mallinckrodt no. 8176.

10.15 Stannous chloride solution - Add 25 g of $SnCl_2 \cdot 2 H_2O$ per 100 mL of 20% v/v hydrochloric acid. Mix well to dissolve. Prepare fresh weekly. Discard if precipitation occurs.

10.16 Mercury stock standard solutions, 1000 ppb - use 2 different suppliers for solutions "A" and "B": Ultra Scientific no. ICP-080, Fisher no.SM114, Mallinckrodt no. H548.

10.17 Mercury working standard solutions, 1 ppm (1000 ppb) - "A": Add 0.15 mL of concentrated $HNO_3$ to a 100-mL volumetric flask and add 50 mL of reagent water. Aliquot 0.10 mL of mercury stock standard solution "A" into the flask, dilute to the mark, and mix. Repeat for mercury spiking standard "B", except using mercury stock standard solution "B". Prepare fresh monthly.

## 11.0 PROCEDURE

**NOTE:** Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the appropriate log book(s) ***before beginning analysis***.

11.2.1 Method Validation Study - A method validation study must be performed, including a method detection limit determination. (Refer to section 10.7 for details.)

### 11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.2.1 For Method Blanks:

- Liquid samples - Aliquot 100 mL of reagent water into a BOD bottle.
- Solid samples - Place 0.5 g of clean sand into a BOD bottle.
- Wipe samples – Place a 15cm Whatman 41 filter paper into a BOD bottle.

11.2.2 For Laboratory Control Samples (samples contain 1.0 ppb Hg).

- Liquid samples - Aliquot 100 mL of reagent water into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.
- Solid samples - Place 0.5 g of clean sand into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.
- Wipe samples – Place a 15cm Whatman 41 filter paper into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.

11.2.3 For Test Samples:

- Aqueous liquids - Aliquot a 100-mL portion of well-mixed sample in a BOD bottle.
- Non-aqueous liquids - Transfer a representative 10-50 mL aliquot of well-mixed sample into a BOD bottle. Add reagent water to the bottle to bring the total volume to 100 mL.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well-mixed before pouring a representative aliquot. The analyst should use his/her own judgement in determining the proper aliquot size so as not to exceed 20% non-aqueous liquid in the sample. If less than 100 mL is used, add reagent water to bring the total volume to 100 mL.
- Solid samples - A representative 0.5 g portion of sample is weighed and placed in a BOD bottle (for samples with a high water content, be sure the sample is mixed thoroughly). For samples of mixed solid types, particle size reduction and mixing may be required to ensure that a representative sample is analyzed.
- Wipes samples - The entire wipe is placed into the BOD bottle, and the sample container rinsed into the BOD bottle with about 5ml of water..

11.2.4 For Matrix Spike Samples (samples have 1.0 ppb Hg added):

- Liquid samples - Aliquot two additional 100-mL portions of one sample, making sure to sample as homogeneous a mixture as possible. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each replicate. Mark as MS and MSD.

- Non-aqueous liquids - Transfer two additional representative 10-50 mL aliquots of well-mixed sample into BOD bottles. Add reagent water to the bottles to bring the total volume to 100 mL. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle, and label as MS and MSD.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well-mixed before pouring a representative aliquot. Do not exceed 20% non-aqueous liquid in the sample. If less than 100 mL is used, add reagent water to bring the total volume to 100 mL. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle, and mark as MS and MSD.
- Solid samples - Two additional representative 0.5 g portions of one sample are weighed and placed into BOD bottles. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle and label as MS and MSD.
- Wipes samples - Two additional wipes are placed into two BOD bottles (1 each), and the sample containers rinsed with a minimum amount of reagent water. Accurately aliquot 0.10 mL of spiking standard "B" into each bottle. Mark as MS and MSD.

## 11.3 PREPARATION OF CALIBRATION AND CHECK STANDARDS

11.3.1 Add 100 mL of reagent water to each of 6 BOD bottles. Aliquot 0.00, 0.05, 0.10, 0.15, 0.20, and 0.25 mL of mercury working standard "A" into the bottles to produce a set of calibration standards of 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 ppb mercury.

11.3.2 Add 100 mL of reagent water and 0.10 mL of mercury spiking standard "B" to a BOD bottle, producing a 1.0 ppb check standard.

## 11.4 DIGESTION OF LIQUIDS

See section 11.5 for digestion of solids.

**CAUTION:** The heated reaction in the BOD bottles produces gases and steam which will cause significant pressure. Bottle stoppers should be wet with water prior to placing in the bottle necks to prevent freezing up and allowing the samples to outgas.

11.4.1 Carry all standards and samples through all steps of the digestion procedure.

11.4.2 Add 5 mL of concentrated $H_2SO_4$ and 2.5 mL of concentrated $HNO_3$, mixing after each addition.

11.4.3 Add 15 mL of potassium permanganate solution. Allow samples to stand for 15 minutes. If the purple color fades, add additional permanganate, noting in the log book how much additional permanganate has been added. Once the purple color has persisted for 15 minutes, proceed to the next step.

11.4.4 Add 8 mL of potassium persulfate solution, and place in the water bath for 2 hours at 95-100°C. Monitor and record the temperature of the water bath initially and every 30 minutes, adding boiling water to the bath as necessary to keep the bath level above the level of sample in the BOD bottles.

11.4.5 After the heating period, remove the sample bottles, cool, and add 6 mL of hydroxylamine hydrochloride solution (reduces excess permanganate).

## 11.5 DIGESTION OF SOLIDS

See section 11.4 for digestion of liquids.

**CAUTION:** The heated reaction in the BOD bottles produces gases and steam which will cause significant pressure. Bottle stoppers should be wet with water prior to placing in the bottle necks to prevent freezing up and allowing the samples to outgas.

11.5.1 Carry all standards and samples through all steps of the digestion procedure.

11.5.2 For solids: Add 10 mL of 50% *aqua regia*. Heat in a water bath at 95°C for 2 minutes.

11.5.3 Cool, and add 50 mL of reagent water and 15 mL of potassium permanganate solution.

11.5.4 Place in the water bath for 30 minutes at 95-100°C.

11.5.5 After the heating period, remove the sample bottles, cool, and add 6 mL of hydroxylamine hydrochloride solution (reduces excess permanganate). Add 50 mL of reagent water and mix.

## 11.6 ANALYTICAL PROCEDURE

11.6.1 Refer to the manufacturer's instruction manual for instrument set-up and operation. See Appendix B for a condensed list of operating instructions.

11.6.2 Calibration - The analyst will be prompted for the calibration blank and each standard in turn. The digests will be processed and analyzed by the instrument and the resultant absorbencies used to construct a calibration curve. The curve must have a correlation coefficient of 0.995 or greater to be valid. If not, the instrument will attempt a second calibration. If this fails, the operator must stop the run and determine the problem and correct before continuing.

11.6.3 A typical batch is analyzed according to the following protocol:

1) Calibration blank - result must be < detection level (0.0002 ppb);
2) Initial check standard - result must be within ± 10%
3) Repeat check standard (optional) - same as check standard;
4) High calibration standard - result must be within ± 10%, or within established control limits;
5) Method blank - result must be < detection level (0.0002 ppb);
6) LCS samples - result must be within ± 15%, or within established control limits;
7) Unspiked matrix test sample;

8-9) Matrix spikes - result must be within ± 25%, or within established control limits;

10+) Balance of test samples. Include a check standard every 10 samples (or less) - the check standard must be ± 20%, or the run paused, problem corrected, and any samples run since the last passing check standard re-analyzed.

**Note:** At the end of each analytical run, a calibration blank and check standard must be analyzed. The acceptance criteria is the same as discussed above.

**NOTE:** Samples with a high level of suspended solids may require settling or filtration prior to analysis to prevent blockage of the pump tubing.

11.6.4 If a sample analysis is significantly high out of range, and "poisoning" of the system is suspected, a reagent blank should be analyzed repeatedly until it produces results below the reporting limit. If this isn't accomplished, the system is cleaned, recalibrated, and the affected samples reanalyzed.

11.6.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The absorbance for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:

- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
- the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
- the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where: $C_x$ = Concentration of the sample
$S_B$ = The analytical signal for the sample and water solution (corrected for the blank)
$V_S$ = Volume of the standard solution added
$C_S$ = Concentration of the standard solution added
$S_A$ = The analytical signal for the sample and standard solution (corrected for the blank)
$V_S$ = Volume of the sample added to each solution.

Note: $V_S$ and $C_S$ should be chosen so that $S_A$ is roughly twice $S_B$ on the average. It is best if $V_S$ is made much less than $V_X$ , and thus $C_S$ is much greater than $C_X$, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

## 11.7 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may be calculated and reported.

11.7.1 Liquid Samples:

$$mg/L\ Hg = \frac{analyzed\ concentration \times dilution\ factor \times 100 / volume\ used\ (mL)}{1000}$$

$$detection\ limit\ (DL, mg/L) = \frac{0.2 \times 100 / volume\ used\ (mL)}{1000}$$

11.7.2 Solid Samples:

$$mg/kg\ Hg = \frac{analyzed\ concentration \times dilution\ factor \times 100 / weight\ used\ (g)}{1000}$$

$$detection\ limit\ (DL, mg/L) = \frac{0.2 \times 100 / weight\ used\ (g)}{1000}$$

The dilution factor is 1, unless additional dilution of the sample was done.
"1000" is the conversion factor for ppb to ppm (mg/L).

11.7.3 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.7.4 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. See Appendix C for glassware cleaning instructions. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 13.0 REFERENCES

13.1 EPA Methods 245.1: Mercury (Manual Cold Vapor Technique), and 245.5: Mercury in Sediment (Manual Cold Vapor Technique).
13.2 Method 3112: Metals by Cold-Vapor Atomic Absorption Spectrometry, Section B (Mercury); *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992.
13.3 Methods SW-846 - 7470A: Mercury in Liquid Waste (Manual cold-vapor technique); and 7471A: Mercury in Solid or Semisolid Waste (Manual cold-vapor technique).
13.3 Great Lakes Analytical Quality Assurance Program Manual.
13.4 Great Lakes Analytical Chemical Hygiene Plan.
13.5 Great Lakes Analytical SOP for Login Department.
13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

See Great Lakes Analytical's Quality Assurance Program Manual.

## APPENDIX A.

## METHOD EXCEPTIONS.

A.1 A semi-automated continuous-flow mercury vapor (hydride generator) is used to produce the cold mercury vapor. The automatic nature of the peristaltic pump and mixing manifold provides much enhanced stability and consistency in absorbance readings.

A.2 A calibration range more appropriate to the detection levels required and concentrations of routine samples has been selected at 0.0 to 2.5 ppb.

A.3 For solids, a single 0.5 g portion of sample is used for the analysis. Past performance of P.E. samples and replicate data has shown this procedure to produce accurate and precise results.

A.4 The dead air space in the BOD bottle does not need to be purged before processing the sample through the cold-vapor generator because the final reaction does not occur in the BOD bottle.

# APPENDIX B.

## CONDENSED FLAA OPERATING INSTRUCTIONS

B.1 Sequence:
- Modify an existing sequence
- OK

B.2 Select sequence:
- Mercury 05/27/97, Hex Chrome
- OK
- 4 Hg Vapor, 99 Cr Flame Hexachrome
- Error protocol
- Next
- Exit and switch to instrument window
- OK

B.3 Optimize:
- Rescale
- Instrument zero

B.4 Return:
- Start autorun
- Metal - Matrix - Date
- Analyst's intitials
- OK
- Prompt Present Rinse
- OK
- Calibrate 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 ppb

# APPENDIX C.

## METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

Copy #: 335.4 -____

# GREAT LAKES ANALYTICAL

## STANDARD OPERATING PROCEDURE

## FOR

## THE DETERMINATION OF TOTAL CYANIDE, REACTIVE CYANIDE, AND CYANIDE AMENABLE TO CHLORINATION IN LIQUIDS AND SOLIDS

## GLA 335.4 BG

Revision 2.1

Approved By:

Department Manager: _____ Date: 5/27/99

Quality Assurance Manager: _____ Date: 5/27/99

Laboratory Director: _____ Date: 5/28/99

# 1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the handling, digestion, and distillation of liquid and solid samples for the analysis of total cyanide, reactive cyanide (weak-acid dissociable cyanide), and cyanide amenable to chlorination. This SOP is an interpretation of EPA Method 335.4, Standard Methods no. 4500-$CN^-$, and SW-846 Methods 9010B and 9012A.

## 1.1 MATRICES

This SOP may be used for drinking, ground, surface and saline waters, domestic and industrial waste, (solid, and mixed samples). Concentration range for samples is typically 5 to 1000 µg/L. Higher concentrations may be determined by sample dilution. Samples are preserved by addition of 2 mL of 10 N sodium hydroxide per liter and refrigeration.

**NOTE:** Distillates and solutions produced for this SOP are only applicable for the analysis method specified and are unacceptable for any other anionic or cationic analyses.

## 1.2 REGULATORY APPICABILITY

40 CFR 121

# 2.0 SUMMARY

Sulfuric acid is added to samples. Cyanide is released from the sample as volatile hydrocyanic acid (hydrogen cyanide, or HCN) and absorbed in a gas scrubber containing sodium hydroxide. Cyanide is then converted to cyanogen chloride (CNCl) by reaction with chloramine-T. CNCl forms a red-blue dye color upon the addition of a pyridine-barbituric acid reagent. The absorbance of this dye is measured at 580 nm.

For the analysis of total cyanide, the sample is treated for interferents and then refluxed with sulfuric acid. For the determination of cyanides amenable to chlorination, duplicate samples are portioned out. One sample is treated with excess chlorine (as calcium hypochlorite) for one hour. The excess hypochlorite is destroyed with sodium arsenite and total cyanide determined for both treated and untreated samples. The amenable cyanide is the total cyanide less the residual cyanide determined on the chlorinated sample.

# 3.0 SAFETY

## 3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents.

## 3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

### 3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

### 3.4 METHOD SPECIFIC CHEMICALS

Cyanide is acutely toxic, and in the presence of acid produces highly toxic and volatile HCN (hydrocyanic acid) fumes. All handling of cyanide solutions and salts will be performed with proper gloves and ventilation. All fumes produced by the distillation procedure will be evacuated to an appropriate hood or ventilation source. When performing the amenable cyanide preparation, cyanides react with chlorine to produce CNCl (cyanogen chloride) which is extremely toxic. All amenable cyanide preparations will be performed in a fume hood.

Pyridine is a toxic organic which has a permeating, irritating odor. It is readily absorbed through the respiratory tract and skin. Operations involving large amounts of pyridine will be carried out in a fume hood and proper gloves should be worn. Waste from the analytical process containing pyridine should be covered with parafilm to minimize volatilization of the material.

## 4.0 INTERFERENCES

4.1 Several different interferences are encountered with this method. Most are removed by the distillation process. Those interferences requiring pre-treatment or special treatment of the sample are addressed below.

4.2 Sulfides produce hydrogen sulfide during the distillation which adversely affects colorimetric, titrimetric, and electrode procedures. Samples are tested for sulfides with lead acetate paper. Bismuth nitrate solution is added to samples testing positive for sulfides to remove the interference.

4.3 Oxidizing agents such as chlorine decompose most cyanides. Samples are tested for oxidizers with KI-starch paper. Samples exhibiting positive results for oxidizers are treated with ascorbic acid until a negative test for oxidizers is obtained.

4.4 Nitrate and nitrite may produce a high bias to results. These ions produce nitrous acid which in turn can react with certain organic compounds to produce oximes. These oximes decompose to generate HCN. Interference from nitrates and nitrites is removed by the addition of sulfamic acid to the sample.

4.5 Carbonate in high concentrations may affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when acid is added before distillation. Calcium hydroxide may be used to preserve such samples.

## 5.0 RECORD KEEPING

5.1 The analyst is responsible for keeping accurate and up-to-date records of all distillations and analyses performed.

5.2 Total Cyanide Log Book

A log book will be maintained for all cyanide distillations and determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume or weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Data reviewer's signature and date
- Calibration standard identifiers and concentrations
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final distillate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out. Examples of a log book cover page and reagent preparation sheets are provided in Appendix A of this SOP.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

# 6.0 QUALITY CONTROL

## 6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 10% frequency (*i.e.* one set with every batch of ten or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

## 6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

## 6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of ten or less samples (*i.e.* minimum 10 % frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% (10% for drinking waters) of the known value.

## 6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 10% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

## 6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

## 6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

## 6.7 METHOD OF STANDARD ADDITIONS

The method of standard additions is used for the analysis of all samples that have matrix interferences such as sulfides. This procedure involves adding equal volumes of sample to a reagent water blank and to a standard. The higher the degree of accuracy needed, the greater the number of standard additions. The analytical signal for each of the prepared solutions is plotted on the vertical axis, with the corresponding standard concentrations plotted on the horizontal axis. When the resulting line is extrapolated back to zero analytical signal, the point at which the line crosses the horizontal axis is the concentration (absolute value) of the sample. The results are considered valid if:

- the plotted curve is linear over the concentration range of concern (slope should be less than 20% different than the slope of the calibration curve).
- the effect of the interference does not vary as the ratio of analyte concentration to sample matrix changes and the standard addition responds in a similar manner as the analyte.
- the determination is free of spectral interferences and corrected for nonspecific background interference.

For a single-addition method, the concentration would be calculated as follows:

$$C_x = \frac{S_B V_S C_S}{(S_A - S_B) V_X}$$

where: $C_x$ = Concentration of the sample
$S_B$ = The analytical signal for the sample and water solution (corrected for the blank)
$V_S$ = Volume of the standard solution added
$C_S$ = Concentration of the standard solution added
$S_A$ = The analytical signal for the sample and standard solution (corrected for the blank)
$V_S$ = Volume of the sample added to each solution.

Note: $V_S$ and $C_S$ should be chosen so that $S_A$ is roughly twice $S_B$ on the average. It is best if $V_S$ is made much less than $V_X$ , and thus $C_S$ is much greater than $C_X$, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

## 6.8 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (e.g. a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

# 7.0 SAMPLE MANAGEMENT

**7.1** The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

**7.2** Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "AUTO". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

# 8.0 METHOD VALIDATION

## 8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Control Manual.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

## 8.2 INTERNAL AUDITS AND PERFORMANCE EVALUATION SAMPLES

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Plan.)

## 8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

## 9.0 EQUIPMENT

9.1 Glassware required for each distillation set-up:
- 500-mL round bottom boiling flask.
- Two-neck Claisen adapter with 24/40 ground glass joints.
- Allhin condenser with 24/40 ground glass joints.
- Tubing adapter with PTFE stopcock.
- 125-250 mL gas scrubbing bottle.
- Gas scrubber/stopper with fritted end.
- 300-mm thimble top tube funnels.
- 100-250 mL volumetric flasks.
- 100-250 mL graduated cylinders.

9.2 Heating mantle(s) for 500-mL round bottom flasks with adjustable temperature control.
9.3 Tygon tubing for connecting glass apparatus.
9.4 Analytical balance capable of weighing to the nearest 0.1 grams.
9.5 Lachat Quikchem AE Auto analyzer - capable of delivering and reacting samples and reagents for automated continuous flow analysis, including:
- Sampling device.
- Multi-channel pump.
- Reaction/mixing manifold for cyanide.
- Colorimetric detector.
- Data acquisition device (computer).

9.6 Lead acetate paper, Fisher no. 14-862.
9.7 Potassium iodide (KI)-starch paper, Fisher no. 14-860.
9.8 Teflon-coated stir bars and magnetic stir plate.

## 10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II or equivalent (DI water).
10.2 Ascorbic acid - crystal, ACS, analytical reagent grade, or USP, Mallinckrodt no. 1852.
10.3 Bismuth nitrate pentahydrate - $Bi(NO_3)_3 \bullet 5\ H_2O$, Fisher no. B337, or Mallinckrodt no. 0256.
10.4 Bismuth nitrate, 0.062 M - Dissolve 30.0 g of $Bi(NO_3)_3 \bullet 5\ H_2O$ into 100 mL of reagent water in a 1-L reagent bottle. Add 250 mL of glacial acetic acid while stirring. Dilute to 1 L with reagent water and mix.
10.5 Calcium hypochlorite - $Ca(OCl)_2$, Fisher no. C100.
10.6 Calcium hypochlorite, ~5% - Dissolve 50 g of $Ca(ClO)_2$ in 1000 mL of reagent water. Store protected from light exposure for up to one month.
10.7 Sodium hydroxide - NaOH pellets, Fisher no. S318, or Mallinckrodt no. 7708. **CAUTION:** Sodium hydroxide is corrosive.
10.8 Sodium hydroxide solution, 1.25 N - Dissolve 50 g of NaOH per liter of reagent water.
10.9 Sulfamic acid - $H_2NSO_3H$, Fisher no. A295, or Mallinckrodt no. 1931.
10.10 Sulfamic acid solution, 0.4 N $H_2NSO_3H$ - Dissolve 40 g of $H_2NSO_3H$ in 1 L of reagent water.
10.11 Sulfuric acid - concentrated $H_2SO_4$, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.12 Sulfuric acid, 18 N - Carefully dilute 500 mL of concentrated $H_2SO_4$ into 500 mL of reagent water, or use purchased 50% v/v (Fisher LabChem no. LC25640).
10.13 Magnesium chloride hexahydrate - $MgCl_2 \bullet 6\ H_2O$, Fisher no. M33, or Mallinckrodt no. 5958.

10.14 Magnesium chloride solution - Dissolve 510 g of $MgCl_2 \bullet 6\ H_2O$ per liter of reagent water.
10.15 Sodium arsenite - $NaAsO_2$, Fisher no. S225I. **CAUTION:** Arsenic compounds are toxic!
10.16 Sodium arsenite solution, 2% (w/v) $NaAsO_2$ - Dissolve 2 g of $NaAsO_2$, into 100 mL of reagent water.
10.17 Stock cyanide solutions - Calibration and spiking/check standards are prepared separately from independent sources of potassium cyanide (KCN, for example Fisher no. P223I, Mallinckrodt no. 6881). **CAUTION: Poison!** Standards expire one year from date of preparation.
- Weigh ~260 mg of potassium cyanide (KCN) and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm $CN^-$. Label this solution calibration standard "A". Actual concentration is determined titrimetrically per Appendix B.
- Weigh ~260 mg of potassium cyanide (KCN) and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm $CN^-$. Label this solution calibration standard "B". Actual concentration is determined titrimetrically per Appendix B.

10.18 Standard silver nitrate solution(s), 0.01-0.02 N $AgNO_3$ - for example, Fisher (LabChem) no. 22630, Mallinckrodt no. H394. Solutions from two sources required.
10.19 p-Dimethylaminobenzalrhodanine - Aldrich no. 11,458-8, or Mallinckrodt no. 2754.
10.20 Acetone - reagent grade, Fisher no. A18.
10.21 Indicator solution - Dissolve 20 mg of p-dimethylaminobenzalrhodanine in 100 mL of acetone.
10.22 Barbituric acid - Aldrich no. 18,569-8, or Mallinckrodt no. 2046.
10.23 Pyridine - $C_5H_5N$, Fisher no. P368. **CAUTION:** Strong odor.
10.24 Hydrochloric acid - concentrated HCl, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.25 Pyridine-barbituric acid reagent - Weigh 15 g of barbituric acid into a 1-L reagent bottle. Rinse down the sides and wet with about 100 mL of reagent water. In a fume hood, add 75 mL of pyridine, and mix thoroughly. Carefully add 15 mL of concentrated HCl and mix. Transfer to a 1000-mL volumetric flask and dilute to the mark with reagent water. Mix until all of the barbituric acid has dissolved. This solution should have a pale straw color. A dark orange or yellow indicates improper preparation and reagent needs to be re-prepared. This solution is stable for six months.
10.26 Sodium phosphate, monobasic, monohydrate - $NaH_2PO_4 \bullet H_2O$, Fisher no. S369.
10.27 Sodium dihydrogen phosphate buffer, 1 M - Dissolve 138 g of $NaH_2PO_4 \bullet H_2O$ in 1 L of reagent water. Store refrigerated.
10.28 Chloramine-T, Mallinckrodt no. 0614-58.
10.29 Chloramine-T solution - Dissolve 2.0 g of chloramine-T in 500 mL of reagent water.
10.30 Glacial acetic acid, $CH_3COOH$, Fisher no. A38.
10.31 Dilute acetic acid - Dilute 1 mL of glacial acetic acid to 100 mL with reagent water.

## 11.0 PROCEDURE

**NOTE:** Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

### 11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.2.1 For Method Blanks:
- Liquid samples - Aliquot 250 mL of reagent water into a clean 500-mL round bottom flask.
- Solid samples - Weigh 10 g of clean sand (20 g for reactive cyanide) into a clean 500-mL round bottom flask. Add 250 mL of reagent water.

11.2.2 For Laboratory Control Samples (samples contain approximately 400 ppb $CN^-$).

- Liquid samples - Aliquot 250 mL of reagent water into a clean 500-mL round bottom flask. Accurately aliquot 1.0 mL of spiking standard 'B' into the flask.
- Solid samples - Weigh 10 g of clean sand (20 g for reactive cyanide) into a clean 500-mL round bottom flask. Add 250 mL of reagent water. Accurately aliquot 1.0 mL of spiking standard 'B' into the flask.

11.2.3 For Test Samples:

- Aqueous liquids - A representative 250 mL aliquot of sample is placed into a clean 500-mL round bottom flask. (If high cyanide content is expected, a proportionally smaller sample can be used. Bring the total volume to 250 mL with reagent water.)
- Non-aqueous liquids - Transfer a representative 25 g portion of well mixed sample into a clean 500-mL round bottom flask. Add 225 mL of reagent water to the flask.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well mixed before pouring a representative aliquot. The analyst should use his/her own judgment in determining the proper aliquot size so as not to exceed 20% (50 mL) of non-aqueous portion of sample. If less than 250 mL is used, reagent water is added to bring the total volume to 250 mL.
- Solid samples - A representative 10 g portion of sample is weighed into a clean 500-mL round bottom flask. Use 20 g of sample for reactive cyanide determinations. Mixed solids may require particle size reduction to assure a homogeneous sampling of all solids in the sample. Add 250 mL of reagent water to the flask. (If high cyanide content is expected, a proportionally smaller sample can be used.)

11.2.4 For Matrix Spike Samples (samples have approximately 400 ppb $CN^-$ added):

- Liquid samples - Measure two additional 250 mL aliquots of one sample, making sure to sample as homogeneous a mixture as possible. Accurately aliquot 1.0 mL of spiking standard "B" into the replicate samples, and mark them as MS and MSD.
- Solid samples - Weight two additional aliquots of one sample, making sure to sample as homogeneous a mixture. Add 250 mL of reagent water to each flask. Accurately aliquot 1.0 mL of spiking standard "B" - into the replicate samples, and mark them as MS and MSD.

11.2.5 Add stirring bars to samples for reactive cyanide determinations (proceed to section 11.5). Add several boiling chips to samples for distillation (proceed to section 11.3).

**NOTE: Samples for total and amenable cyanide determinations must be screened for sulfide and oxidants!**

## 11.3 SAMPLE SCREENING AND PRE-TREATMENTS

11.3.1 Sulfide:

- Screening is performed by placing several drops of a water sample or of the soil/water slurry on a strip of lead acetate paper which has been moistened with dilute acetic acid. A blackening of the paper indicates the presence of sulfides, and the sample must be treated prior to distillation.
- Pre-treat for sulfides by adding 25 mL of bismuth nitrate solution to the sample and mixing for 5 minutes before starting distillation.

11.3.2 Oxidants:

- Screening is performed by placing several drops of a water sample or of the soil/water slurry on a strip of KI starch paper. A darkening or blue color of the paper indicates the presence of chlorine or other oxidants, and the sample must be treated prior to distillation.
- Pre-treat for oxidants by adding small amounts of ascorbic acid to the sample until a negative result is obtained for the KI-starch paper test. Then add an additional ~0.5 g of ascorbic acid.

11.3.3 Samples screened for sulfides and oxidants are now ready for distillation and/or pre-treatment for cyanide amenable to chlorination (sections 11.4 and 11.5).

## 11.4 CHLORINATION OF SAMPLES

**This treatment only for samples of cyanides amenable to chlorination.**

**NOTE:** This procedure must be performed under amber or reduced lighting. Potassium ferricyanide may decompose under fluorescent lighting or sunlight, producing a positive result for cyanide amenable to chlorination.

11.4.1 Prepare two identical replicate samples for total cyanide. Reserve one replicate for a normal total cyanide analysis.

11.4.2 To the other replicate, in a hood, add small amounts of a 5% calcium hypochlorite solution to the sample while stirring on a magnetic stir plate until an excess of hypochlorite is present, as indicated by a positive KI-starch paper test.

11.4.3 Test the sample every ten minutes and maintain an excess of hypochlorite on the sample for one hour.

11.4.4 Add 1 mL portions of 0.1 N sodium arsenite solution until KI-starch paper indicates no residual chlorine. Add an additional 5 mL of 0.1 N sodium arsenite solution to ensure an excess of reducing agent.

11.4.5 Samples screened for oxidants, sulfides, and treated for amenable cyanides are now ready for distillation (section 11.5).

## 11.5 DISTILLATION PROCEDURE

11.5.1 Assemble each digestion unit in accordance with Figure 1.

11.5.2 Aliquot 50 mL of 1.25 N NaOH into each scrubber bottle, and add enough reagent water to cover the fritted glass bubbler on the end of the stem. Close the stopcock valve on the adapter.

11.5.3 When all scrubbers have been prepared, switch on the vacuum pump and adjust the stopcock valve on each set-up to allow a slow stream of air to pass through the system. Adjust the valve so that roughly two bubbles per second enter the 500 mL digestion flask through the end of the tube funnel.

11.5.4 Add distillation reagents:

- For total and amenable cyanide only: 25 mL of sulfamic acid solution to each sample through the tube funnel. Allow to mix for three minutes minimum.
- 50 mL of 18 N $H_2SO_4$ (25 mL for reactive cyanide) to each sample.
- For total and amenable cyanide only: 20 mL of 2.5 M $MgCl_2$ solution to each sample.

11.5.5 For total and amenable cyanide only, distill the samples (for reactive cyanide, stir the samples at room temperature and allow air flow to continue for 30 minutes):

- Switch on heating mantles and set to high.
- Note the time that each sample begins boiling to the nearest 5 minute interval, and note on the flask with a marking pen.
- Continue refluxing for one hour. Turn off mantle(s) and continue the airflow for at least 15 minutes.

- Allow the boiling flask to cool, dislodge the tube funnel stopper and close the vacuum valve.

11.5.6 Quantitatively transfer the scrubber solutions into clean 250-mL volumetric flasks and dilute to the mark with reagent water. The distillates are now ready for automated (LACHAT) or manual colorimetric (Milton-Roy SPEC 20) analysis.

**NOTE: If samples are not to be run on the same day distilled, the distillates are stored in the refrigerator, or transferred to plastic sample cups and stored refrigerated.**

## 11.6 PREPARATION OF CALIBRATION AND CHECK STANDARDS

11.6.1 Calibration standards are prepared by serial dilutions of stock standard "A". Note that final concentrations of the standards depend upon the concentration of the calibration source standard as determined titrimetrically (Appendix B). *(Sodium hydroxide is added to each standard to matrix match the standards with the distillates.) Prepare standard set per Table 1.

Table 1.
**Preparation of Calibration Standards.**

| Standard Level | Volume Stock Standard (mL) | Final Volume (mL) | Volume 1.25 N NaOH (mL) | Approx. $CN^-$ Concentration (ppb) |
|---|---|---|---|---|
| A | 1.0 | 100 | 20 | 1000 |
| B | 0.5 | 100 | 20 | 500 |
| C | 0.2 | 100 | 20 | 200 |
| D | 0.1 | 100 | 20 | 100 |
| E | 0.05 | 100 | 20 | 50 |
| F | 0.025 | 100 | 20 | 25 |
| G | 0.010 | 100 | 20 | 10 |
| H | 0.00 | 100 | 20 | 0 |

11.6.2 Check Standard - A Check Standard is prepared fresh daily. The check standard is prepared by aliquoting 0.5 mL of Spiking Source Standard "B" into a 100-mL volumetric flask, adding 20 mL of 1.25 N NaOH, diluting to the mark with water, and mixing. This check standard contains approximately 500 ppb cyanide. Reserve the previous check standard as it will also be evaluated with the run as the "old check standard".

NOTE: At client request, high and low standards may be distilled along with samples. The concentrations of the distilled check standards should be ± 10% of the undistilled standards.

## 11.7 OPERATION OF THE LACHAT ANALYZER

11.7.1 Power up the Lachat analyzer in accordance with the manufacturer's instructions. **Allow the system to warm up at least 15 minutes.**

11.7.2 Install the cyanide manifold, sample loop, and filter, making sure that all connections have been made and properly tightened.

11.7.3 Place the reagent uptake tubes in their appropriate reagent bottles and prime the system while checking for leaks.

11.7.4 Pour an aliquot of each Calibration Standard (A-H) into 6-mL disposable culture tubes and place in the corresponding sampler positions (see Table 2).

Table 2.
**Positions of Samples in the Analyzer.**

| Position | Sample | Position | Sample | Position | Sample |
|---|---|---|---|---|---|
| 1 | Blank | 5 | High Cal Std | 9 | Matrix Spike |
| 2 | Blank | 6 | Blank | 10 | Matrix Spike Duplicate |
| 3 | Old Check Std | 7 | Method Blank | 11 | Matrix Sample |
| 4 | New Check Std | 8 | LCS | 12 | Blank |

11.7.5 The remaining samples from the batch are loaded into the sampler with a Check Standard and Calibration Blank every ten or less samples, including the QC spikes and samples. Each analytical run must end with the analysis of a blank and check standard.

11.7.6 Select "ANALYSIS METHOD SELECT AND DOWNLOAD" and select the "CYANIDE - NO BOUND" program. The system will now call up its operating parameters and set a baseline. Observe this baseline on the instrument screen. If it appears unstable or drifts upward or downward, allow more warm up time for the instrument. Other baseline anomalies may be indicative of other system problems and the operations manual should be referenced and the Department Manager notified.

11.7.7 After the baseline has stabilized, select "SUBMIT" and "CALIBRATE NOW". The system will re-zero the baseline and perform a calibration. The data system will perform a linear least squares regression analysis based on the segments selected. All usable segments must have an $R^2$ fit of .9950 or better to be deemed acceptable. If the calibration fails to meet this criteria, the system will indicate this and require analyst review of the calibration prior to acceptance. The reason for the calibration failure should be determined and the calibration re-run if necessary.

**NOTE:** It is recommended that the analyst review the calibration data before running samples, even if the calibration has passed. A good mathematical curve fit might not produce accurate results near the detection limit/baseline, and the curve might necessarily need to be re-run even though the fit was acceptable due to anomalous baseline response.

11.7.8 After the calibration has been passed and accepted by the analyst, select "IDENTIFICATION". Remove the default end run marker (..) by overwriting with two spaces. Escape to exit.

11.7.9 Select "RUN CURRENT TRAY". Follow the instructions to initiate the run using "Y" for start tray, "96" for number of samples, and "1" for tray start position.

11.7.10 The analyzer will run the samples and determine the cyanide concentrations using the newly created calibration curve. For this data to be acceptable, the criteria in Table 3 must be met.

**NOTE:** Batch data not within specified limits may be re-analyzed later in the run. The ICB, ICV, and High Calibration Standard must pass to continue with the run. Any dilution factors used on samples are to be noted in the log book and on the run sheet. Samples falling outside the high end of the curve may be diluted with 0.25 N NaOH and re-run.

In addition, if the old versus new check standards fail to meet the above criteria and fresh working standard preparation does not resolve the discrepancy, the stock standards should be re-titrated to verify the cyanide concentration of BOTH calibration and spiking standard. If the concentration has changed, the standards and logs must be updated as if a new preparation had been performed, but using the original expiration date(s).

| Table 3. **Run Data Acceptance Criteria.** | | |
|---|---|---|
| **Sample Type** | **Acceptance Parameter** | **Action Upon Parameter Failure** |
| **Blanks** | < Reporting D.L. or <M.D.L (spec case) | Re-analyze blank - if still fails, recalibrate and re-run - if still fails prepare fresh, re-cal and re-run |
| **Old Check Std** | ± 10 % of known value | Re-analyze check std - if still fails, recalibrate and re-run - if still fails prepare fresh and re-run |
| **New Check Std** | ± 10 % of known value | Must be within 10 % of old check std, else prepare fresh calibration standards and re-calibrate |
| **High Cal Std** | ± 10 % of known value | Re-analyze standard - if still fails, recalibrate and re-run - if still fails prepare fresh, re-cal and re-run |
| **Method Blank** | < Reporting D.L. or <M.D.L (spec case) | Re-analyze - if contamination is suspected, redigest - if proven, redigest batch if hits |
| **LCS** | within established control limits or 85-115 | If out of control, re-analyze - if still fails, redigest - if still fails, re-cal - if still fails, redigest set |
| **Matrix Spike** | within established control limits and RPD | Evaluate data, **must obtain managerial approval to report**, initiate corrective action |
| **Matrix Spike Duplicate** | within established control limits and RPD | Evaluate data, **must obtain managerial approval to report**, initiate corrective action |
| **Sample Results** | within 10% of calibration curve high standard | Dilute sample with cal blank solution and re-run |
| **Continuing Check Stds** | ± 20 % of known value | Correct problem, reanalyze all samples since last good CCV - if fails, re-cal and re-run |
| **Continuing Blanks** | < Reporting D.L. or <M.D.L (spec case) | Correct problem, reanalyze all samples since last good CCB - if fails, re-cal and re-run |

## 11.8 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may calculated and reported.

11.8.1 Liquid Samples:

$$mg\ CN^-/L = \frac{Lachat\ result \times dilution\ factor \times final\ distillate\ volume\ (mL)}{initial\ sample\ volume\ (mL) \times 1000}$$

11.8.2 Solid Samples:

$$mg\ CN^-/L = \frac{Lachat\ result \times dilution\ factor \times final\ distillate\ volume\ (mL)}{initial\ sample\ weight\ (g) \times 1000}$$

(The dilution factor is 1, unless additional dilution of the sample was done at the instrument.)

11.8.3 For amenable cyanide:

*Cyanide amenable to chlorination =*
*Total cyanide (untreated sample) - Total cyanide (treated sample)*

**NOTE:** The cyanide amenable to chorination test is subject to a matrix interference in the presence of iron-cyanide complexes. If the result of the treated sample is higher than the total cyanide result but is within precision limits for the method, the result should be reported as "no determinable quantities of cyanide amenable to chlorination". If the difference is greater than precision limits, the nature of the interference should be determined and accounted for in the reported result.

11.8.4 Percent Recovery Calculation for spiked samples and LCS:

$$\% \text{ Recovery} = \frac{\text{Calculated Spike Conc.} - \text{Conc. of Sample}}{\text{Spike Conc. Added}} \times 100\%$$

11.8.5 Relative Percent Difference (%RPD) for duplicate analyses:

$$\%\text{RPD} = \frac{|\text{Conc. of } 1^{st} \text{ Analysis} - \text{Conc. of Duplicate Analysis}|}{(\text{Conc. of } 1^{st} \text{ Analysis} + \text{Conc. of Duplicate Analysis})/2} \times 100\%$$

## 12.0 MAINTENANCE AND TROUBLESHOOTING

### 12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

### 12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

## 13.0 REFERENCES

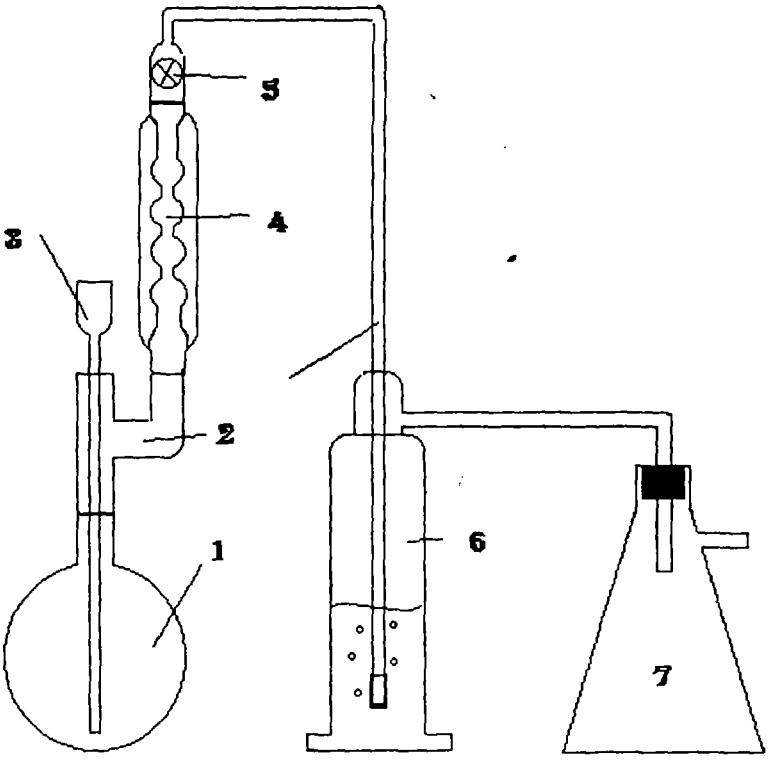
13.1 Method 335.4: Cyanide, Total (Semi-automated colorimetry).
13.2 Methods 4500-$CN^-$: A, B, C, E, G, and I: Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.3 Methods SW-846 - 9010B (Revision 2): Total and Amenable Cyanide, Distillation; and 9012A (Revision 1): Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation).
13.4 Methods SW-846 (Revision 2) - Chapter Seven: Characteristics Introduction and Regulatory Definitions, Section 7.3.3: Reactive Cyanide (pages 4-8).
13.5 Great Lakes Analytical Quality Assurance Program Manual.
13.6 Great Lakes Analytical Chemical Hygiene Plan.
13.7 Great Lakes Analytical SOP for Login Department.
13.8 Great Lakes Analytical SOP for Hazardous Sample Management.

## 14.0 DEFINITIONS

See the Great Lakes Analytical Quality Assurance Program Manual

**Figure 1.**

**Apparatus for cyanide distillation.**




1. 500-mL Round-bottom flask
2. Claissen adapter
3. Thistle top tube funnel
4. Allihn condenser
5. Stopcock/connecting tubing
6. Gas scrubber/absorber
7. Vacuum trap (outlet to vacuum pump)

# APPENDIX A.

## EXAMPLES OF DOCUMENTATION SHEETS.

A.1 Log book cover page.

A.2 Reagent preparation log sheet - 10.17: Stock calibration/reference standards.

A.3 Reagent preparation log sheet - 10.10: Sulfamic acid solution.

A.4 Reagent preparation log sheet - 10.14: Magnesium chloride solution.

A.5 Reagent preparation log sheet - 10.27: Phosphate buffer solution.

A.6 Reagent preparation log sheet - 10.25: Pyridine-barbituric acid reagent.

A.7 Cyanide determinations run log.

# Book nnn

# TOTAL CYANIDE
# (TOTAL AND AMENABLE CYANIDES)

## GLA 335.4 BG

## PREPARATION AND ANALYSIS
## LOG BOOK

Date Started: _____

Date Stopped: _____

This is a controlled document (properly identified and logged):

QA Manager: _____ Date: _____

## GREAT LAKES ANALYTICAL

# REAGENT PREPARATION LOG SHEET

## GLA 335.4 BG CYANIDE: STOCK CALIBRATION/REFERENCE STANDARDS

| Preparation of Cyanide Stock Standard Solutions (10.17) | | | | | |
|---|---|---|---|---|---|
| Weigh ~260 mg of KCN and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm $CN^-$. Label the solution calibration standard "A" or "B" as appropriate. Actual concentrations are determined titrimetrically per Appendix B. | | | | | |
| **Reagent** | **Weight (g)** | **Manufacturer** | **Lot No.** | **GLA No.** | **Rec'd Date** |
| KCN "A" | | | | | |
| KCN "B" | | | | | |
| NaOH | | | | | |
| **Silver nitrate** | **Concentration (N)** | | | | |
| - #1 | | Mallinckrodt | | | |
| - #2 | | Ricca | | | |
| Analyst/date: | | | | | |

| Titration of Cyanide Stock Standard Solution "A" | | | | |
|---|---|---|---|---|
| **Date** | **Initials** | **Silver Nitrate** | **Volume Titrant (mL)** | **Calculated Cyanide (mg/L)** |
| | | #1 | | |
| | | | | |
| | | | | |
| | | #2 | | |
| | | | | |
| | | | | |
| **Average cyanide concentration =** | | | | |

| | |
|---|---|
| GLA Code No.: | Exp. Date: |

| Titration of Cyanide Stock Standard Solution "B" | | | | |
|---|---|---|---|---|
| **Date** | **Initials** | **Silver Nitrate** | **Volume Titrant (mL)** | **Calculated Cyanide (mg/L)** |
| | | #1 | | |
| | | | | |
| | | | | |
| | | #2 | | |
| | | | | |
| | | | | |
| **Average cyanide concentration =** | | | | |

| | |
|---|---|
| GLA Code No.: | Exp. Date: |

REAGENT PREPARATION LOG SHEET

## GLA 335.4 BG CYANIDE: REAGENTS FOR DISTILLATIONS

| Preparation of Sulfamic Acid Solution (10.10) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Dissolve 40 g of sulfamic acid ($H_2NSO_3H$) in 1 L of reagent water. | | | | | | | | | |
| | **Reagent** | **Manuf.** | **Lot No.** | **GLA No.** | **Rec'd Date** | **Weight (g)** | **GLA Code No.** | **Expiry** | **Analyst Initals/Date** |
| 1 | Sulfamic acid | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
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REAGENT PREPARATION LOG SHEET

## GLA 335.4 BG CYANIDE: REAGENTS FOR DISTILLATIONS

| Preparation of Magnesium Chloride Solution (10.14) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Dissolve 510 g of magnesium chloride ($MgCl_2$) in 1 L of reagent water. | | | | | | | | | |
| | **Reagent** | **Manuf.** | **Lot No.** | **GLA No.** | **Rec'd Date** | **Weight (g)** | **GLA Code No.** | **Expiry** | **Analyst Initals/Date** |
| 1 | $MgCl_2$ | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
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**GREAT LAKES ANALYTICAL**

REAGENT PREPARATION LOG SHEET

## GLA 335.4 CYANIDE: REAGENTS FOR DISTILLATIONS

| Preparation of Phosphate Buffer Solution (10.27) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Dissolve 138 g of sodium phosphate dibasic ($NaH_2PO_4$) in 1 L of reagent water. Store refrigerated. | | | | | | | | | |
| | **Reagent** | **Manuf.** | **Lot No.** | **GLA No.** | **Rec'd Date** | **Weight (g)** | **GLA Code No.** | **Expiry** | **Analyst Initals/Date** |
| 1 | $NaH_2PO_4$ | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
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**GREAT LAKES ANALYTICAL**

REAGENT PREPARATION LOG SHEET

## GLA 335.4 CYANIDE: REAGENTS FOR ASSAY

### Preparation of Pyridine-Barbituric Acid Reagent (10.25)

Weigh 15 g of barbituric acid (A) into a 1-L reagent bottle. Rinse down the sides and wet with about 100 mL of reagent water. In a fume hood, add 75 mL of pyridine (B), and mix thoroughly. Carefully add 15 mL of concentrated HCl (C) and mix. Transfer to a 1000-mL volumetric flask and dilute to the mark with reagent water. Mix until all of the barbituric acid has dissolved. This solution is stable for six months.

| Reagent | | Manuf. | Lot No. | GLA No. | Rec'd Date | |
|---|---|---|---|---|---|---|
| A-1 | Barbituric acid | | | | | |
| -2 | | | | | | |
| B-1 | Pyridine | | | | | |
| -2 | | | | | | |
| C-1 | conc. HCl | | | | | |
| -2 | | | | | | |

| | Barb. Acid (A) | Weight A (g) | Pyridine (B) | conc. HCl. (C) | GLA Code No. | Expiry | Analyst Initals/Date |
|---|---|---|---|---|---|---|---|
| 1 | A-1 | | B-1 | C-1 | | | |
| 2 | | | | | | | |
| 3 | | | | | | | |
| 4 | | | | | | | |
| 5 | | | | | | | |
| 6 | | | | | | | |
| 7 | | | | | | | |
| 8 | | | | | | | |
| 9 | | | | | | | |
| 10 | | | | | | | |
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| 14 | | | | | | | |
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## GLA 335.4 CYANIDE RUN LOG

Page n of N

| Batch No.: | | | Matrix: | | |
|---|---|---|---|---|---|
| | Analyst | Date | Spiking/Cal. Standard | Conc. | Expiry |
| Sample Prep.: | | | GLA- | | |
| Sample Analysis: | | | GLA- | | |
| Carrier: | Buffer: | | Reagent: | Chlor-T: | |

| | Client GLA Sample ID | Amount used (mL/g) | Dilution Factor | Lachat Reading | Lachat Result | Calculated Result (mg/L $CN^-$) | Recovery (%) |
|---|---|---|---|---|---|---|---|
| 1 | MB | | | | | | |
| 2 | LCS | | | | | | |
| 3 | MS | | | | | | |
| 4 | MSD | | | | | | |
| 5 | | | | | | | |
| 6 | | | | | | | |
| 7 | | | | | | | |
| 8 | | | | | | | |
| 9 | | | | | | | |
| 10 | | | | | | | |
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GREAT LAKES ANALYTICAL

# APPENDIX B.

## DETERMINATION OF CYANIDE CONCENTRATIONS BY TITRATION.

B.1 Cyanide in solution forms a complex with added silver ion. After all cyanide becomes bound, excess silver ion is detected by the silver sensitive indicator p-dimethylaminobenzalrhodanine, which changes from a yellow to a salmon color.

B.2 Aliquot 50 mL of the approximately 100 ppm cyanide stock solution to a beaker suitable for titration, add 5 mL of 1.25 N NaOH, a stir bar, and 0.5 mL (10 drops) of indicator solution. Provide moderate stirring.

B.3 Place silver nitrate ($AgNO_3$) titrant #1 into a 10-mL buret, and titrate the diluted cyanide solution to the first change in color from a canary yellow to a salmon hue. Record the volume used.

B.4 Prepare and titrate 5 additional aliquots of cyanide stock standard solution, 2 using titrant #1 and 3 with titrant #2.

B.5 Prepare a blank by adding 5 mL of 1.25 N NaOH to 50 mL of reagent water. Add 0.5 mL (10 drops) of indicator solution. Plate on the magnetic stirrer and titrate. Record the volume of titrant used.

B.6 Calculate the concentration of cyanide in the stock standard from each titration by:

$$mg\ CN/L = \frac{(A - B) \times normality\ titrant \times 10}{0.0192}$$

Where:
A = volume of titrant used for cyanide stock standard solution.
B = volume of titrant for blank.
10/0.0192 is the conversion factor for normality silver nitrate to mg/L (ppm) cyanide, and accounting for the volume of cyanide stock standard used.

B.7 Calculate the average concentration determined.